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Chemistry. — *The Essential Oil from the Leaves of Caesalpinia Sappan L.* (Provisional communication). By Prof. P. VAN ROMBURGH.

(Communicated at the meeting of September 26, 1925).

Many years ago [1]) I obtained by steam distillation of the leaves from Caesalpinia Sappan L. (the tree that yields the well known Sappan wood) 0.16—0.2 % of a pleasant smelling, almost colourless essential oil. The specific gravity of the oil was 0.825/28° and it showed a strong dextro-rotation. The figures found for the rotation differed for samples extracted upon different days, this may have been due, partly to the age of the leaves and partly to the duration of the distallations. The extreme values were + 75° and + 100°30′ in a 2 dcm. tube.

The bulk of the oil distilled at 170°, another fraction was collected up to 250°, a viscous colourless residue remaining in the flask. When the fraction that boiled at 170° was redistilled, it appeared to polymerise partially. After repeated fractionation the liquid boiling at 170° showed a dextro-rotation of 125° in a 2 dcm. tube.

The odour of the oil was similar to that of phellandrene, and on account of the considerable quantity of phellandrene nitrite that separated when the oil was treated with sodium nitrite and acetic acid, (the well known reaction for that hydrocarbon) one would be inclined to consider phellandrene as the principal constituent of the oil.

During the year 1902, I extracted a greater quantity of the oil, obtaining from 139 kg. of fresh leaves, 410 c.c., i.e. a yield amounting to almost 0.25 %. The specific gravity (0.841/26°) was found to be higher than that of the oil extracted six years before. It showed a rotation of + 76° in a 2 dcm. tube.

After the oil had been kept in a well closed bottle for over 23 years, it was found that the specific gravity had risen to 0.865/22° and that contents of the bottle had become more viscous and slightly darker in colour.

The low specific gravity (0.825/28°) of the previous oil sample, had already made me doubt whether phellandrene was indeed its principal constituent. In order to ascertain whether this was the case, the oil was subjected to more careful investigation, and was first fractionated in vacuo. About one-third of the oil distilled between 65—70°/20 mm. and had a specific gravity of 0.813/22°. When this fraction was heated

[1]) Report on the State of 's Lands Plantentuin (Botanical Gardens) at Buitenzorg (Java), 1896, p. 48.

with sodium on the water bath and finally distilled of this metal, neither the boiling point nor the specific gravity of the liquid had altered.

By means of a second fractionation, the liquid was divided into two fractions having a difference of rather more than 1° in their boiling points. In both cases the specific gravity was found to be 0.813/22°. The liquid of specific gravity 0.813/22°, which I shall now call "hydrocarbon Caes", showed a rotation of + 59°59′ in a 1 dcm. tube, while the original oil extracted during 1902 now showed a rotation of + 34°19′ in a 1 dcm. tube. The "hydrocarbon Caes" had a refractive index of $n_D^{16^\circ} = 1.473$ and gave the following results on analysis:

	C 88.06 %	H 11.67 %
	88.23	11.71
calculated for $C_{10}H_{16}$	88.2	11.8

In order to study the influence of distillation at ordinary pressure on this hydrocarbon, 10 c.c. were fractionated with the following results:

0.5 cc	B.P. 165°	d_{17}°	0.819
3 „	„ 165—168	d_{17}°	0.821
5 „	„ 168—169	d_{17}°	0.823

The residue in the flask boiled much higher, evidently polymerisation had taken place.

By refractionation of the combined fractions in vacuo, I obtained a liquid having $d_{17} = 0.818$.

Like phellandrene, the hydrocarbon Caes gives upon treatment with nitrous acid, a beautifully crystalline nitrite, which was prepared according to the method WALLACH and GILDEMEISTER[1]). The melting point was found to be 112° and thus agrees with the melting point of the nitrite prepared from *d*-*α*-phellandrene by WALLACH[2]).

Through the kindness of the well known firm of SCHIMMEL & Co, of Miltitz, at my request two samples of phellandrene were placed at my disposal, for which I tender here my sincere thanks. This enabled me to compare my nitrite with the one obtained by WALLACH, and moreover, to compare in many respects the hydrocarbon Caes, with the samples of phellandrene. The latter came from the laboratory of Prof. GILDEMEISTER; one being *d*-*α*-phellandrene from bitter fennel oil, and the other being *l*-*α*-phellandrene from Eucalyptus oil.

It was now found that the nitrite from the *d*-*α*-phellandrene when mixed with the nitrite prepared from the hydrocarbon Caes, did not cause a lowering of the melting point, so that this hydrocarbon either contains this phellandrene, or, an olefinic terpene which by the action of nitrous acid is converted into the nitrite of this phellandrene after ring formation. We can accept the presence of an olefinic terpene upon

[1]) Ann. **246**, 282 (1888).
[2]) Ann. **336**, 15 (1904).

other grounds, for WALLACH[1]) gives 0.844/19° for the specific gravity of *d*-*a*-phellandrene. Therefore another hydrocarbon having a lower specific gravity must be present in the hydrocarbon Caes., accepting that it contains phellandrene. As there we known no cyclic terpenes having a lower sp. gv. than 0,844, and whereas olefinic terpenes like myrcene and ocimene, have a sp. gv. of about 0.803, the hydrocarbon Caes., if it is a mixture, should contain about 60 % of an olefinic, perhaps optically active terpene.

It is also remarkable that equal quantities of the two phellandrenes that I received from SCHIMMEL & Co., and of our hydrocarbon, gave about the same quantities of nitrite by the action of nitrous acid.

We attempted to prepare a crystalline compound from the hydrocarbon Caes. by the action of hydrochloric acid, but no solid substance could be obtained, the liquid however turned brown.

If an olefinic terpene were actually present, it should be possible to add two atoms of hydrogen to this terpene by means of the action of sodium and boiling ethyl alcohol, just as SEMMLER succeeded in doing with myrcene, and C. J. ENKLAAR, in this laboratory, with ocimene.

20 grams of the hydrocarbon and 100 grams of absolute alcohol at boiling point, were treated with 30 grams of sodium. The hydrocarbon obtained by the reduction had the following constants:

boil.p.$_{15}$: 63°, $d_{15}^{21} = 0.800$ $\quad a_D = +15.48$ [2]) $\quad n_D^{16} = 1.4581$.

Analysis gave:	C 87.54 %	H 12.61 %
	87.39	12.70
Calculated for $C_{10}H_{18}$:	86.96	13.04.

The hydrogenated compound readily absorbed bromine. From this addition product, which was at first liquid, in the course of some weeks a few crystals separated, and after it had been inoculated with crystals of dihydroocimene tetrabromide[3]). The crystals thus obtained melted at 89.5—90.5° and the melting point was not lowered when they were mixed with a preparation of ENKLAAR's dihydroocimene tetrabromide, which melts at 91—92°.

The hydrocarbon Caes. was also treated with acetic acid and dilute sulphuric acid, according to the method of POWER and KLEBER, which was also applied by ENKLAAR for the hydration of ocimene.

The viscous alcohol obtained after the hydration boiled at 115—122°/30 mm. The quantity obtained did not allow of further fractionation. It had the following constants:

$$d_{15}^{16} = 0.890 \qquad n_D^{16} = 1.484.$$

An analysis gave results that indicated the presence of a mixture of

[1]) Loc. cit. p. 12.

[2]) Calculated from the rotation of an alcoholic solution of 25 %.

[3]) A preparation from the laboratory and made by Dr. C. J. ENKLAAR.

83 % of terpene alcohol with 17 % of hydrocarbon. By treatment with phenylisocyanate a liquid urethane was obtained. (For comparison, 50 grams of ocimene were hydrated in the same way. The ociminol so obtained gave with phenylisocyanate a good yield of a urethane having a melting point of 72° as was also found by ENKLAAR).

If *d*-*α*-phellandrene is treated with acetic acid and dilute sulphuric acid, a liquid is obtained which boils above 160° at 20 mm., has a sp.gv. of 0.94, and does not give an urethane. Probably a polymerisation product is formed.

The hydrocarbon Caes., and also the hydrogenation product prepared from it, proved to be highly variable in composition, when they were kept in a flask closed with a cork. It was found that the sp. gv. of a preparation of the hydrocarbon having 0.813/21°, had increased to 0.856/16° after 4 weeks, and that the specific gravity of a preparation of the hydration product had increased from 0.800/21° to 0.825/22°.

When the changed Caes. hydrocarbon was again fractionated, it was possible to obtain from it a fraction which had $d_{15°}$ 0.819, and which after hydrogenation gave a product having b.p./22 mm. 73—74° and $d_{23°}$ 0.798.

For the present, the experiments described above lead to the conclusion that the hydrocarbon Caes. is either a mixture of *d*-*α*-phellandrene (or perhaps another terpene) with an olefinic terpene or such an olefinic terpene.

The material with which to continue my researches is wanting. I hope however, in order that I may be able to elucidate several obscure points, to receive some new material from Java, or to obtain it there myself.

My thanks are due to Mr. J. A. VAN MELSEN, cand. chem., who has assisted me with great zeal in these experiments.

Utrecht, *Org. Chem. Lab. of the University.*

Chemistry. — *Formation of derivatives of dihydrobenzimidazole and tetrahydrochinoxaline by the action of acetic anhydride and zinc chloride on nitroderivates of alkylanilines.* By Prof. P. VAN ROMBURGH and H. W. HUYSER.

(Communicated at the meeting of June 26, 1926).

Some years ago, at this laboratory, Mr. HOEJENBOS, chem. doct^{s}., allowed acetic anhydride and zinc chloride to react on 3.6.dinitrodiethylaniline, in order to introduce an acetylgroup, and thus to obtain an acetophenone derivative. Though this introduction did not succeed with dimethylaniline, Mr. HOEJENBOS obtained a beautifully crystalline product (mp. 127°), with the study of which, however, he could not proceed.

Some time ago we have again taken up the investigation of this substance, and at the same time have studied the action of zinc chloride on other nitro-derivates of dialkyanilines.

It was found that not only the nitro-compound, mentioned above, but also the 2.4.dinitrodiethylaniline, as well as the 3.6.- and the 2.4.dinitro-, and also the 3.4.6.trinitro-dimethylaniline gave easily crystallisable reaction products.

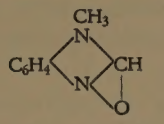
The analyses of all these compounds, which were obtained as principal products in the reaction, indicated that one acetyl group had been introduced into the molecule, and that at the same time one mol of water had been removed.

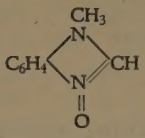
We thought at first that the acetylgroup which had been introduced, had replaced one atom of hydrogen in the benzene nucleus, but we had to give up this opinion, because a prolonged investigation proved that this acetylgroup could easily be eliminated by heating with 10 % caustic potash solution, and could easily be reintroduced in some of the compounds which contained no acetyl group. The action of potash did not eliminate amines, as is the case with the unsubstituted nitro-products.

The analyses of the acetylfree compounds pointed to substances which had been formed out of the original substance by the removal of the elements of one mol of water.

The question we had to solve was: what groups from the molecule had taken part in the formation of water. It was obvious to assume that the nitro- and dialkylaminogroup, being ortho-situated, had to be considered.

The nitrated dimethylaniline derivates could then yield nitro-compounds of a substance to which might be given the following formulae:


(I)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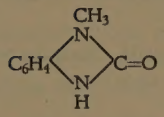
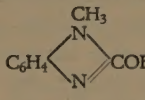

(III)


(IV)

III—IV are tautomeric compounds.

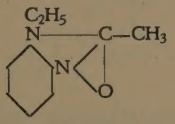
The first and the second do not contain a mobile hydrogen atom which could be replaced by acetyl. The two last, on the contrary, do. In these substances the oxygen-atom could perhaps be replaced by chlorine with simultaneous elimination of HCl, by the action of phosphorouspentachloride. This proved indeed to be the case with the anhydrocompound out of 3 . 6.- as well as out of 3 . 4 . dinitrodimethylaniline.

Finally, formula III was confirmed by a synthesis. If, namely phosgene is allowed to react with 4 . nitro 2 . aminomethylaniline a substance is formed which is identical with the anhydro-compound formed from 2 . 4 . dinitrodimethylaniline.

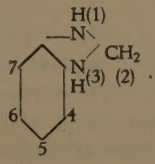
Compounds formed by the reaction of acetic anhydride and zinc chloride on the suitable nitroderivates of dimethylaniline are therefore nitroderivatives of 1 . methyl 2 . oxo 1 . 2 . dihydrobenzimidazol [1]).

The products which are formed by the reaction of acetic anhydride and zinc chloride on nitrated diethylanilines are, as regards the results of the analyses, i.e. the empirical formulae, completely analogous with those of the methylderivates. If we assume this to be true, there are two possibilities:

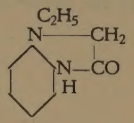
1. The hydrogen of the CH_2-group of the ethylgroup can react with elimination of water, and there will appear a compound of the type



2. The hydrogen of the CH_3-group of the ethylgroup can react, and

[1]) 1.2 dihydrobenzimidazol: 

there will be formed a compound of the type

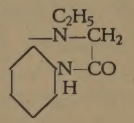


In contrast with the methylcompounds the ethylderivatives are soluble in dilute acids, and insoluble in dilute alkalis.

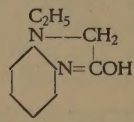
The formation of a nitroso-compound, which easily changes back into the original product by the action of strong hydrochloric acid, makes the second possibility highly probable.

Moreover, if the first formula is taken to be correct, we cannot explain why these substances so easily form an acetyl derivate, or which hydrogen-atom would be substituted in this case.

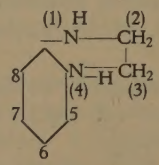
By reason of what has been said above we are justified in deriving the anhydrocompounds obtained out of the dinitrodiethylanilines from a substance with the formula:



or its tautomeric form:



They are thus derivatives of 1.2.3.4 tetrahydrochinoxaline:



therefore: nitrated 1 . ethyl . 3 . oxo . 1 . 2 . 3 . 4 . tetrahydroquinoxalines.

1. *The reaction of acetic anhydride and zinc chloride on some nitroderivatives of dimethylanilines.*

In the following reactions, 0.5 parts of zinc chloride and 2 parts of acetic anhydride were taken with 1 part of the substance, which, with the dinitroderivatives, was heated under a reflux condenser during 4 or 5 hours. Then the somewhat viscous reaction mixture, was diluted with a little alcohol and poured into about 40 parts of water. The separated

product was dried and boiled with benzene. The substance crystallised from the benzene solution upon cooling.

a. 3 . 6 . dinitrodimethylaniline gives 6 . nitro 1 . methyl 3 . aceto 2 . oxo 1 . 2 . dihydrobenzimidazole (A), which melts at 185°—186° C.

Analysis:	C 51.19,	51.02	H 4.05,	3.75	N 18.18,	18.01
Calculated for $C_{10}H_9N_3O_4$	C 51.06		H 3.83		N 17.87	

Determination of mol. weight (according to LANDSBERGER) 216, 219 calc. 235.

The substance forms almost white needles, the cristals however contain $^1/_4$ mol of benzene (found 7.9 and 7.6, calc. 8.2).

If (A) is boiled with caustic alkali the acetylgroup is replaced by hydrogen, and a substance is formed which melts at about 272° C., slightly brown, long needles (out of alcohol), which crumble into shorter crystals after a few days.

This substance is an anhydrocompound from the original product, namely 6 . nitro 1 . methyl 2 . oxo 1 . 2 . dihydrobenzimidazole (B).

Analysis:	C 49.53,	49.83	H 3.73,	3.79	N 21.93,	21.72
Calc. for $C_8H_7N_3O_3$	C 49.74		H 3.63		N 21.76	

(B) was also formed when we tried to oxidize (A) with CrO_3 in acetic acid solution.

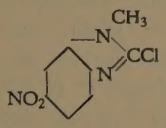
The substance is soluble in caustic potash; with strong caustic potash a potassium compound is precipitated.

Treatment of (A) with iron in concentrated hydrochloric acid reduces the nitro-group, with elimination of the acetylgroup: 6 . amino 1 . methyl 2 . oxo 1 . 2 . dihydrobenzimidazole (C) is formed, which crystallizes as a hydrochloride with one mol of H_2O.

Analysis:	C 44.20,	44.22	H 5.77,	5.75	N 19.30,	19.23
	Cl 16.42	16.47				
Calc. for $C_8H_9N_3$ 0.HCl + H_2O	C 44.14		H 5.52		N 19.31	Cl 16.32

The determination of water gave 8.21 calc. 8.28.

By the reaction of phosphorouspentachloride on the anhydrocompound (B) dissolved in phosphorousoxychloride we get:



that is: 6 . nitro 1 . methyl 2 . chlorobenzimidazole.

Analysis:	N 19.65,	19.62	Cl 17.0			
Calc. for $C_8H_6N_3O_2Cl$	N 19.86		Cl 16.8			

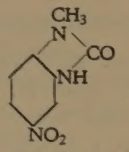
b. 2 . 4 . dinitrodimethylaniline gives a compoud (mp. 175°—176° C.) when treated with acetic anhydride and zinc chloride.

Analysis:	C 51.17,	51.33	H 3.92,	3.99	N 18.00,	17.86
Calc. for $C_{10}H_9N_3O_4$ (e.g. $NO_2C_6H_3$ [NCH_3 . CO . $NCOCH_3$])	C 51.06		H 3.83		N 17.87	

This compound is the 5 . nitro 1 . methyl 3 . aceto 2 . oxo 1 . 2 . dihydrobenzimidazole (D).

Like the analogous 6 . nitro derivative this substance changes into the acetylfree anhydrocompound by heating with diluted caustic soda . mp . 300°.

Determination of nitrogen 21.86 and 21.87 N
Calc. for $C_8H_7N_3O_3$ 21.76 N.

The formula may be written: 

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So it is 5 . nitro 1 . methyl 2 . oxo 1 . 2 . dihydrobenzimidazole (E).

By reduction with iron and hydrochloric acid (E) passes into the aminocompound analogous to (C), which crystallised as a hydrochloride with 1 mol of H_2O (mp . 320°—330° C. under decomposition).

Determination of chlorine: Cl 16.54 and 16.47
Calc. for $C_8H_9N_3O . HCl + H_2O$ Cl 16.29.

By treating (E) with phosphorouspentachloride in a solution of phosphorousoxychloride colourless needles are formed of 5 . nitromethyl 2 . chlorobenzimidazole.

Analysis: Cl 16.90, 16.91 N 19.70, 19.53
Calc. for $C_8H_6N_3O_2Cl$ Cl 16.78 N 19.86

By the reaction of phosgene on 4 . nitro 2 . aminomonomethylaniline, dissolved in benzene, we succeeded in synthesizing (L). The substance obtained had the same mp. as (E) and did not lower the mp. when mixed with it.

By boiling the compound (E) with glacial acetic acid we obtained the compound (D), mp. 175° C.

c. 3 . 4 . 6 . trinitrodimethylaniline also reacts with acetic anhydride and zinc chloride, but much slower. Instead of from 4 to 5 hours it is necessary to heat for 72 hours. The melting point of the reaction product obtained, which dissolves in alkali, and is then precipitated again by acids, is 294° C. It does not contain an acetylgroup, but according to the analysis, has the anhydrogroup of the original substance: therefore 5 . 6 dinitro 1 . methyl 3 . oxo 1 . 2 . dihydrobenzimidazole (F).

Analysis: C 40.36, 40.41 H 2.55, 2.89 N 23.69, 23.64
Calc. for $C_8H_6N_4O_5$ C 40.33 H 2.52 N 23.53.

An acetylcompound of this substance is formed when (A) is nitrated with cold nitric acid. The mp. of the substance obtained, 5 . 6 . dinitro 1 . methyl 3 . aceto 2 . oxo 1 . 2 . dihydrobenzimidazole (G) lies at about 191° C.

Analysis: C 42.70, 42.78 H 3.06, 2.88 N 20.08, 20.20
Calc. for $C_9H_8N_4O_6$ C 42.85 H 2.85 N 20.0.

By the reaction of caustic potash, the acetylgroup is substituted by hydrogen, and a product is obtained which has the same mp. and is identical with (F).

2. *The reaction of acetic anhydride and zinc chloride on dinitrodiethylanilines.*

a. Out of 3.6.dinitrodiethylaniline is formed a substance which crystallizes in almost white needles, and which melts at 127°.

Analysis:	C 54.50,	54.55	H 5.20,	5.03	N 16.18,	16.24
Calc. for $C_{12}H_{13}N_3O_4$	C 54.75		H 4.94		N 15.97	

Mol. weight (according to LANDSBERGER) Found 230 and 252, calc. 247.

This substance is 7.nitro 1.ethyl 4.aceto 3.oxo 1.2.3.4, tetrahydroquinoxaline (H).

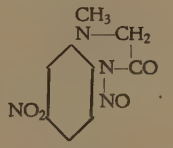
By treating (H) with a 10 % aqueous solution of alkali, the acetylgroup is replaced by hydrogen, and we get again the anhydrocompound of the original substance which melts at 206° C.

Determination of nitrogen. Found 19.08 and 18.96 calc. for $C_{10}H_{11}N_3O_3$: 19.0 N.

This substance is 7.nitro 1.ethyl 3.oxo 1.2.3.4.tetrahydroquinoxaline. (I).

By treating with sodium nitrite in a solution of dilute sulphuric acid we get a nitrosocompound, which easily passes into the anhydrocompound again upon the addition of warm hydrochloric acid.

It is highly probable therefore that the nitroso-compound has the following structure:



b. According to the well known reaction we obtain out of 2.4.dinitrodiethylaniline a compound which melts at 157° C.

Analysis:	C 54.21,	54.30	H 5.18,	5.35	N 19.06,	19.05
Calc. for $C_{10}H_{11}N_3O_3$, that is the original product, less 1 mol. of H_2O	C 54.30		H 4.98		N 19.0.	

This substance will therefore be 6.nitro 1.ethyl 3.oxo 1.2.3.4.tetrahydroquinoxaline. In this case no acetyl derivative was obtained.

The synthesis of these quinoxaline derivatives is still under investigation, and in the Recueil des Travaux Chimiques des Pays-Bas we hope to enlarge upon the results mentioned in this paper.

Utrecht. *Organic-chemical Laboratory of the University.*

Mathematics. — *A Representation of the Congruence of* REYE. By Prof. JAN DE VRIES.

(Communicated at the meeting of September 24, 1927).

1. The congruence van REYE is formed by the twisted cubics k^3 that pass through five fixed points B_k. Through a point M chosen at random there passes one bisecant b of a k^3; let the intersection P of b, with the fixed plane Φ be considered as the *image* of k^3. The curve k_0^3 through M has as images any point of the conic c^2 in which Φ is cut by the cone that projects k_0^3 out of M. The intersection C_k of MB_k is the image of each k^3 that has MB_k as bisecant.

2. The points P of a line l in Φ are the images of the curves k^3 that have the rays of a plane pencil (b) as bisecants. These curves form a surface Δ of which we may find the degree by examining the intersection of Δ with the plane $\beta_{123} = B_1B_2B_3$. If D_{45} is the intersection of of B_4B_5 with the plane λ of (b), B_{45} the intersection of B_4B_5 with β_{123}, E_{45} the intersection of β_{123} with MD_{45}, the conic $B_1B_2B_3B_{45}E_{45}$ together with the line B_4B_5 forms a k^3, of which the bisecant $D_{45}E_{45}$ belongs to the plane pencil (b). The intersection of Δ with β_{123} consists, accordingly, of this conic and the lines B_1B_2, B_2B_3 and B_3B_1; the surface Δ is of the *fifth* degree and has *triple points* in B_k. The image of Δ^5 is the point range on l: as l contains two points of c^2, k_0^3 is a *nodal curve* of Δ^5.

The locus of the pairs of points that the curves k^3 of Δ have in common with the rays of (b), is a curve λ^4 with node M; together with a straight line m it forms the intersection of Δ with the plane λ of (b); m joins the other points of intersection of k_0^3 and the plane λ. Evidently Δ may also be considered as the locus of the curves k^3, that cut a bisecant m of k_0^3.

3. If l passes through the singular point C_1, Δ consists of the quadratic cone K_1^2, that has MB_1 and the four lines B_1B_k as generatrices and a surface Δ_1^3 with four conical points B_k.

The point range on $c_{12} = C_1C_2$ is the image of the figure consisting of the cones K_1^2, K_2^2 and the plane β_{345}. For any conic through B_3, B_4, B_5 and the passage B_{12} of B_1B_2 forms a k^3 with B_1B_2 of which a bisecant $D_{12}E_{12}$ passes through M and cuts Φ in a point of c_{12}.

4. The curves k^3 that cut an arbitrary line g, form a surface Γ^5 with

triple points B_k (§ 2). This contains, therefore, two curves k^3 that also cut MB_k outside B_k, and that, accordingly, have their images in C_k. As g does not generally cut the curve k_0^3 the image of Γ^5 can only meet the conic c^2 in the points C_k. Hence the image curve is a γ^5 with *double points* C_k; it has a *sixth* double point owing to the k^3 that cuts g twice.

Two image curves γ^5 have five points in common outside C_k; these are the images of the five k^3 that cut g and g'. The corresponding surface Γ^5 have the ten lines $B_k B_l$ in common besides these five k^3.

If g rests on k_0^3, γ^5 consists of c^2 and a rational γ^3. If g is a bisecant of k_0^3, γ^5 is replaced by the c^2 which must be counted twice, and a line l.

The surfaces A^5 corresponding to two lines l and l', have a k^3 in common besides the ten lines $B_k B_l$ and the double curve k_0^3; this k^3 is represented in the point $l\,l'$.

5. The k^3 that cut a given conic s^2, form a surface Σ^{10}; for β_{123} contains two conics k^2 through B_1, B_2, B_3 and B_{45} that meet s^2 so that $B_4 B_5$ is a double line of Σ and the intersection of Σ with β_{123} consists of these two k^2 and the double lines $B_1 B_2, B_2 B_3, B_3 B_1$. As B_k is a *sextuple* point on Σ^{10}, there are four k^3 of Σ that have the line MB_k as bisecant. Hence the image curve σ of Σ has five *quadruple* points C_k; as it cannot cut c^2 outside C_k, the image of Σ is a σ^{10}. As there exists a (1,1) correspondence between the point ranges an c^2 and σ^{10}. σ^{10} is rational and has, therefore, six more double points. Accordingly there are six curves k^3 that cut s^2 *twice*.

If s^2 meets the curve k_0^3, σ^{10} is replaced by c^2 and a σ^8 with triple points C_k. If s^2 rests on k_0^3 in two points, the c^2, which must be counted double, is supplemented by a rational σ^6 with double points in C_k and five double points outside c^2 owing to the five k^3 besides k_0^3 that cut the conic s^2 twice.

If s^2 cuts the curve k_0^3 three times, it replaces three of the six k^3 that meet s^2 twice; the remaining three are represented in the double points of the rational σ^4, that together with the c_{22}, which must be counted three times, forms the image of the system Σ.

6. The k^3 that touch a given plane ψ, form a surface Ψ^{10}; its intersection with β_{123} consists of the two conics k^2 that touch ψ and the three double lines $B_1 B_2, B_2 B_3, B_3 B_1$. The base points B_k are again *sextuple* so that the image curve has *quadruple* points in C_k and is a ψ^{10}.

As β_{123} contains two points of contact of figures k^3 that belong to Ψ, the locus of the points of contact of the k^3 touching ψ is a *conic* ψ^2. The plane ψ has also a rational ψ^6 in common with Ψ^{10}; this has ten double points in the intersections of the lines $B_k B_l$.

The image curve ψ^{10} is rational and has, therefore, six double points

outside c^2; these are the images of *six* k^3 that *osculate* the plane ψ. The curves ψ^2 and ψ^6 touch each other in the six points where ψ is osculated by curves k^3.

The surface Ψ^{10} is formed by the curves k^3 that rest on the conic ψ^2; hence it belongs to the surfaces Σ^{10} discussed in § 5. As any plane contains a rational ψ^6 besides a conic ψ^2, Ψ^{10} may also be considered as the locus of the k^3 resting on a ψ^6.

7. An arbitrary conic φ^2 in the plane φ is the image of a system Φ of curves k^3 that have the generatrices of a quadratic cone as bisecants. The image curve γ^5 of the system of the k^3 that cut a line g (§ 4), has ten points in common with φ^2; accordingly the system Φ lies on a surface Φ^{10}.

The line c_{kl} (§ 3) cuts φ^2 in the images of two composite k^3. Consequently Φ^{10} has two conics and three double lines in common with β_{123}; this proves that the surface has sextuple points in the base points B_k. The four points of intersection of φ^2 with c^2 show that the curve k_0^3 is *quadruple* on Φ^{10}.

8. Let Ω be the system of the k^3 that have the generatrices of a quadratic cone ω^2 with vertex O as bisecants; they form an Ω^{10} with *sextuple* points B_k and a *quadruple* curve (the k^3 that passes through O). This surface has ten curves k^3 in common with the surface Λ^5 of the k^3 that rest on a bisecant of k_0^3 (§ 2) and are represented by the points of a line l. This image curve of the system Ω is, therefore, a curve ω^{10}.

As ω^2 contains two generatrices resting on $B_1 B_2$, there lie two conics through B_3, B_4, B_5, B_{12} on Ω^{10}; hence c_{12} has two points besides C_1 and C_2 in common with ω^{10} and B_1 and B_2 are quadruple points. Consequently the image curve γ^5 (C_k^2) has ten points besides C_k in common with ω^{10}; they are the images of the ten k^3 that rest on the line g (§ 4).

The curve ω^{10} has a *sixth* quadruple point; it is the image of the k^3 that passes through O; the singular points of the ω^{10}, as naturally rational, are, therefore, represented by six quadruple points.

Physics. — *The deviation from* LAMBERT's *law for incandescent tungsten and molybdenum.* By C. ZWIKKER. (Communicated by Dr. G. HOLST.)

(Communicated at the meeting of September 24, 1927)

According to LAMBERT's law the amount of light, emitted by an incandescent surface in a direction which makes an angle α with the normal to the surface, is proportional to $\cos \alpha$. Therefore the apparent brightness of a luminous surface is independent of the angle at which we look at it.

WORTHING [1]) has called attention to the fact that the intensity of the light emitted by incandescent tungsten varies considerably from LAMBERT's cosine law. At an angle $\alpha = 75°$ the brightness reaches a maximum, which, according to this author, exceeds that for normal emission by about 16 %.

In a previous paper [2]) I had some reason to doubt the numerical value of this excess. Now new measurements have been performed all of which indeed give a smaller effect than was mentioned by WORTHING.

A tungsten ribbon filament was pyrometered optically at different angles with respect to the normal. The effective wavelength of the light used was in most cases 0.652 μ.

Figure 1 shows the ratio of the brightness at various angles to the normal brightness as a function of the angle α. The three curves refer to three intervals during the seasoning of the ribbon-filament, viz.

curve 1 : the tungsten ribbon filament is not yet recrystallised, it has still the fibrous structure caused by the rolling ;

curve 2 : the ribbon has glowed for some time at a temperature of 2300°K, as a consequence of which it has become much more polished ;

curve 3 : the ribbon has once more glowed during 40 hours at a temperature of 2400° ; it has become ideally polished and for the main part it consists of a single crystal.

In all these three intervals we have performed our measurements at more than one temperature. The effect appeared to be independent of the temperature. In fig. 1 WORTHING's results are indicated by dots, marked

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[1]) Astr. Journ. **36**, 1912, p. 345.
Phys. Rev. **35**, 1912, p. 76.
Report Intern. Comm. of the Illum. 1924.
Astr. Journ. **61**, 1925, p. 146.
Rev. Gén. de l'Électr. **20**, 1926, p. 310.
Jl. Opt. Soc. Am. **13**, 1926, p. 635.

[2]) Diss. Amsterdam 1925, p. 32.
Arch. Néerland, IX, 1925, p. 237

W. The effect, which I find is the more pronounced the better the ribbon is polished, but it remains considerably smaller than WORTHING's values.

For the same unicrystalline tungsten ribbon filament, we have tried to

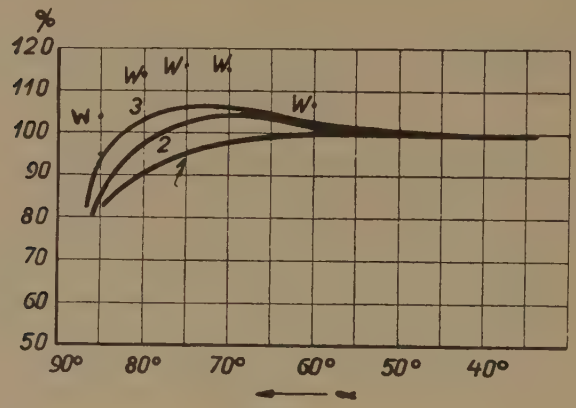

Fig. 1.

find out, whether there is any influence of the direction of emission with regard to the direction of rolling. For three of the four principal directions the effect was the same (see fig. 2 curve *b*), but for the fourth direction the effect was reproduceably found to be smaller (curve *a*). The writer

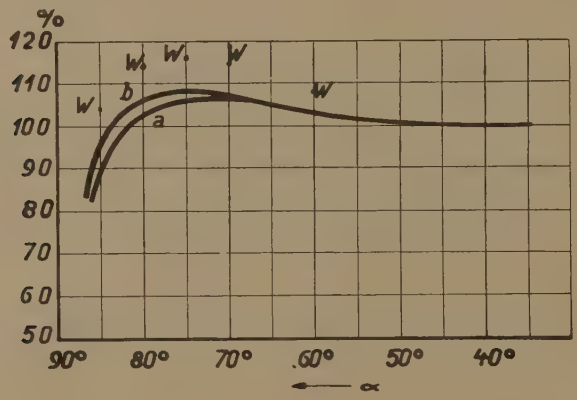

Fig. 2.

believes that here the position of the crystal-axes with respect to the direction and plane of rolling plays a roll. Tungsten has a body-centred cubic lattice. In the rolled ribbon the crystals tend to take up a position so that a (100) plane lies in the rolling plane and a (110) plane lies perpendicularly to the rolling direction. This orientation is however only

approximate, so that the surface consists of steps. Therefore it will make a difference for the effect of the deviation from LAMBERT's law in which direction we look over the surface.

The mean effect for the four principal directions of observation is given in the following table:

α	e/e_0
40°	1.01
50°	1.02
60°	1.03
70°	1.07
75°	1.08
80°	1.04[5]
85°	0.93

The knowledge of the quantity e/e_0 makes it possible to calculate the normal brightness of an incandescent tungsten filament from the total candle power (e.g. the "horizontal" candle power, that is the candle power in a direction perpendicular to the filament axis). Dividing the horizontal candle power by the visible surface, as we should do in case LAMBERT's law would hold strictly, we find too great a value for the normal brightness. The correction is 3 % according to WORTHING, and only 1.6 % according to me. Of even more importance is the correction for the calculation of the normal brightness from the total spherical lightflux of the filament. In this case WORTHING requires a correction of 5 %, the present writer only 2.5 %.

Moreover it is not certain, whether the deviation from LAMBERT's law is constant throughout the whole visible spectrum. The maximum of the light impression lies in the green region and in some cases the deviation from LAMBERT's law is much smaller for green light than it is for red light. This has already been assumed by WORTHING [1]) and was also found by us. We shall have to deal with this question further on. Summarising we can say that, according to our own measurements, the ratio of the mean spherical candle power to the horizontal candle power of a tungsten filament varies less than 1 % from the theoretical value $\frac{\pi}{4} = 0.785$. Indeed, direct measurements of the factor gave a value, which coincided with the theoretical value within the experimental errors [2]).

We have measured the deviation from LAMBERT's law for molybdenum

[1]) Astr. Journ. **36**, 350 (1912).
[2]) Arch. Néerland IX, 239 (1925).

with a ribbon filament which was well-seasoned and well-polished. The filament consisted in this case of a great many little crystals. We could find no difference between the values for the effect in different directions with respect to the rolling direction. Evidently we measure directly the mean effect, because all crystal orientations occur simultaneously. The mean of all our measurements can be seen from fig. 3 and from the there following table ($\lambda = 0.652\ \mu$).

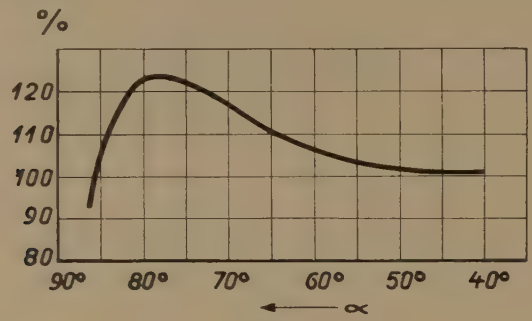

Fig. 3.

angle α	e/e_0
40°	1.01
50°	1.02
60°	1.06[5]
70°	1.17
75°	1.22
80°	1.23
85°	1.06

For green light ($\lambda = 0.541\ \mu$) we found practically the same effect as above for red light. Assuming therefore that the deviation from LAMBERT's law for molybdenum is constant throughout the whole visible spectrum, we compute from these figures that the correction for the normal brightness, when calculated from the horizontal candle power, comes to 3.4 %. On the other hand when calculated from the mean spherical candle power, this correction amounts to 6 %. This last number is in agreement with a note of WORTHING [1]).

Our measurements have been completed by a study of the deviation from LAMBERT's law for the two poralised components of the light emitted. In fig. 4 curve p represents the results, obtained with tungsten and with

[1]) Phys. Rev. **28**, 1926, 195.

light, which has its magnetic vector in the plane of emission. Curve s shows the results for light with the magnetic vector normal to the plane of emission. Denoting the normal emission coefficient by e, the emissivities in the direction α are pe, resp. se. Then, according to KIRCHHOFF's law, the

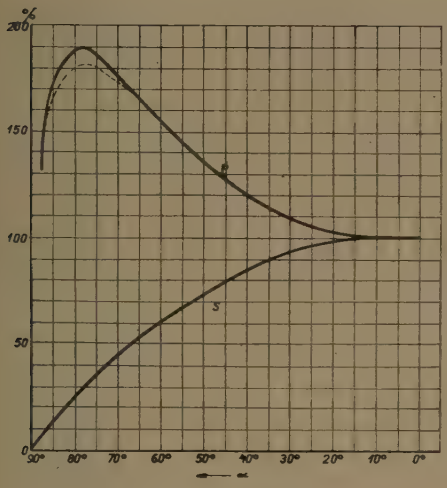

Fig. 4. Tungsten.

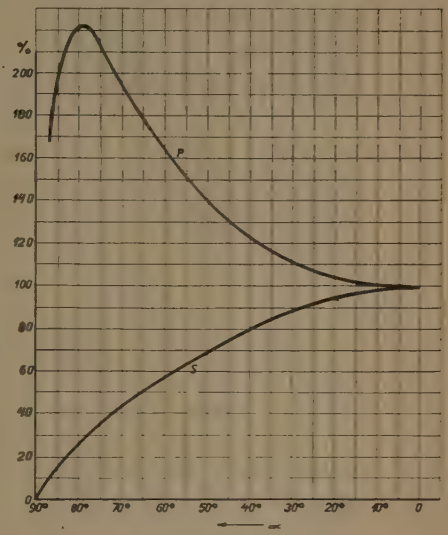

Fig. 5. Molybden.

corresponding reflectivities are $1-pe$ and $1-se$.

Now in first approximation [1])

$$\frac{1-pe}{1-se}=\frac{(m-tg\,\alpha\,sin\,\alpha)^2+\varkappa^2}{(m+tg\,\alpha\,sin\,\alpha)^2+\varkappa^2}$$

where $m =$ refractive index.

$\varkappa =$ coefficient of extinction.

If, for convenience, we put $tg\,\alpha\,sin\,\alpha = a$, then the above equation becomes:

$$(p-s)\,e\,(\varkappa^2+m^2)=\{2-(p+s)\,e\}\,.\,2\,ma-(p-s)\,ea^2.$$

which can be considered as a linear equation with two unknown quantities, viz. $(\varkappa^2 + m^2)$ and m. Substituting the measured values of p and s and the well-known value for e, we get an equation for each value of α. I solved this set of equations graphically by plotting them as straight lines on an $m-(\varkappa^2 + m^2)$ diagram and by determining the point of intersection which is common to all these lines. The position of these straight lines is very sensitive for small errors in α. I only could make the lines pass through one point, if I shifted the scale of the angle α with half a degree. This is a correction which is very probably smaller than the experimental

[1]) See e.g. SCHUSTER—NICHOLSON. The theory of optics. Third edition 1924, p. 276. Other authors (DRUDE, WOOD) put the extinction coefficient equal to $n\varkappa$.

errors. After this correction being applied the optical constants for the unicrystalline tungsten were found as follows:

$$m = 2.96$$
$$\varkappa = 3.36.$$

Fig. 5 shows our measurements performed in polarised light with molybdenum. These measurements are in perfect agreement with measurements of WORTHING [1]) on this same subject. In determining the values of $m^2 + \varkappa^2$ and m in the graphical way as described above, it came out that the straight lines

$$(p - s)\, e\, (\varkappa^2 + m^2) = \{2 - (p + s)\, e\}\, .\, 2\, ma - (p - s)\, ea^2,$$

did not pass through one point so well as this was the case for tungsten. As the most probable values for the optical constants for molybdenum we took:

$$m = 3.75$$
$$\varkappa = 4.25.$$

We have seen that our measurements with molybdenum were in perfect accordance with WORTHING's work. For tungsten, however, our results vary greatly from his. Therefore, I measured the deviation from LAMBERT's law for another tungsten ribbon, well seasoned, but consisting of small crystals, just as the molybdenum ribbon filament, mentioned above. Also the polishing was the same as that of the molybdenum, both these fine-crystallised ribbons being somewhat less polished than the unicrystalline tungsten ribbon filament. As can be seen from the following table, the results obtained with this fine-crystallised tungsten ribbon differed from those, which were obtained with the unicrystalline ribbon:

α	Fine-crystallised			Unicrystalline
	p	s	$\frac{1}{2}(p+s)$	$\frac{1}{2}(p+s)$
10°	1.01	0.99	1.00	1.00
20	1.03[5]	0.96	1.00	1.00
30	1.10	0.91	1.00	1.00
40	1.19	0.83	1.01	1.01
50	1.35	0.73	1.04[5]	1.02
60	1.52	0.61	1.06	1.03
70	1.73	0.47	1.10	1.07
75	1.85	0.38	1.11	1.08
80	1.85	0.28	1.06[5]	1.04[2]
85	1.68	0.15	0.91[5]	0.93

[1]) Jl. of the Opt. Soc. of Am. **13**, 640 (1926).

The *s*-line for the fine-crystallised tungsten lies above the *s*-line for the unicrystalline tungsten and is responsible for the greater deviation from LAMBERT's law.

The two specimens differed still in another respect, viz. the deviation from LAMBERT's law for green light. For fine-crystalline tungsten, just as for molybdenum, the effect is the same for red light and for green light. The unicrystalline tungsten showed hardly any effect in green light. The emissivity exceeded its normal value slightly between $\alpha = 10°$ and $\alpha = 80°$ to a maximum excess of 3 %.

Although the deviation from LAMBERT's law for the second tungsten sample is greater than for the first, I cannot account for the still much greater effect, found by WORTHING. His *p* line reaches a maximum of 204 %, mine never exceeds 190 %.

For completeness I must mention measurements performed by Dr. DE GROOT in this laboratory on tungsten ribbon filaments in natural light (these measurements have not yet been published). His tungsten was not recrystallised, but exceedingly well-polished. The deviation from LAMBERT's law which he found was the same as was found by me for unicrystalline tungsten.

Summarising, we come to the conclusion that, at least for tungsten, the deviation from LAMBERT's law depends on the condition of the surface in a not quite controlable manner. It is evident that a better polishing tends to make the effect smaller.

In conclusion, I tabulate the values for the optical constants, which I have computed from the various measurements. For the normal emissivity has been taken the value 0.44 for tungsten and 0.37 for molybdenum.

Observer	Material	m	$\varkappa$
WORTHING	Tungsten	4.28	3.33
ZWIKKER	Tungsten, unicrystalline	2.96	3.36
ZWIKKER	Tungsten, multicrystalline	2.90	3.35
WORTHING + ZWIKKER	Molybdenum, multicrystalline	3.75	4.25

The writer is indebted to Mr. G. SCHMIDT for his aid in the experimental work.

Natuurkundig Laboratorium der
N. V. PHILIPS' *Gloeilampenfabrieken.*

Eindhoven, September 1927.

Physics. — *On the mean values of straight and curved chords of geometrical bodies.* By P. CLAUSING. (Communicated by Dr. G. HOLST).

(Communicated at the meeting of September 24, 1927).

§ 1. In working out a diffusion-problem connected with the adsorption-phenomenon of the molecules of very rare gases on a glass-wall we found a simple relation between the area of the cross section of an infinite long cylindrical tube, the circumference of this section and the mean distance traversed by a molecule between two collisions with the wall of the tube. It was assumed that the molecules did not collide with each other and that they left the wall according to the "cosine-law". This law corresponds to a random distribution of moving points in space and implies that the number of molecules which passes in unit time through an element of surface in a certain direction, is proportional to $\cos \vartheta$, if ϑ is the angle between the perpendicular to the element and the said direction.

On closer inspection of the derivation of this relation it turned out to be a particular case of a much more general theorem, which can be stated in the following way.

The mean chord of a "body" with "volume" V_m and "area" S_m in a m-dimensional space is given by

$$\bar{\varrho}_m = \lambda_m \cdot \frac{V_m}{S_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with

$$\lambda_m = \frac{1 \,.\, 3 \,.\, 5 \,. \,. \,. \,. \,. \,. \,. \,. \,. \,(m-1)}{2 \,.\, 4 \,. \,. \,. \,. \,. \,. \,. \,. \,. \,(m-2)} \,.\, \pi$$

for even m, and

$$\lambda_m = \frac{2 \,.\, 4 \,.\, 6 \,. \,. \,. \,. \,. \,. \,. \,. \,. \,(m-1)}{1 \,.\, 3 \,.\, 5 \,. \,. \,. \,. \,. \,. \,. \,. \,. \,(m-2)} \,.\, 2$$

for odd m[1]).

The formula (1) also holds for the mean length of the arcs which are

[1]) We find e.g. for a m-dimensional sphere

$$\lim_{m=\infty} \bar{\varrho}_m = 0.$$

cut off from the great circles of a m-dimensional spherical space by a body in this space [1]).

A proof of the theorem for $m = 3$ and non-curved spaces does not offer difficulties. The defininiton of $\bar{\varrho}$ is

$$\bar{\varrho} = \frac{\int_S \int_{\frac{\Omega}{2}} \varrho \cos\vartheta \, d\Omega \, dS}{\int_S \int_{\frac{\Omega}{2}} \cos\vartheta \, d\Omega \, dS}, \quad \ldots\ldots\ldots \quad (2)$$

where ϑ is the angle between the chord ϱ and the normal to the element of surface dS; $d\Omega$ is an element of the complete solid angle Ω. Considering that $d\Omega = d\vartheta \sin\vartheta \, d\varphi$ and that $\varrho \cos\vartheta \, dS$ represents an element of volume dV with base dS and length ϱ, extending in the direction ϑ, we find

$$\bar{\varrho} = \frac{\int_S \int_{\frac{\Omega}{2}} dV \, d\Omega}{S \int_0^{2\pi} d\varphi \int_0^{\frac{\pi}{2}} \sin\vartheta \cos\vartheta \, d\vartheta} = \frac{2V \cdot \frac{4\pi}{2}}{S \cdot 2\pi \cdot \frac{1}{2}} = \frac{4V}{S}, \quad \ldots \quad (3)$$

in agreement with (1). The factor 2 in the numerator in front of V is inserted because in the integration over the total surface S each element dV is counted twice. A similar proof holds for more-dimensional spaces.

§ 2. The second proof of (3), which emerged from our considerations about the said adsorption, is much simpler.

For this purpose we write $\bar{\varrho} = 4V/S$ in the form

$$S \cdot \frac{1}{4} n u \cdot \frac{\bar{\varrho}}{u} = V n \, . \quad \ldots\ldots\ldots \quad (4)$$

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[1]) We find for the area of a segment from a m-dimensional sphere, interpreted as a $(m-1)$-dimensional volume, generally

$$\lim_{m=\infty} \bar{\varrho}_{m-1} = 0,$$

but

$$\bar{\varrho}_{m-1} = \pi R,$$

for each value of $m > 1$, if the segment coincides with half a sphere. R is the radius of the sphere.

n is the number of molecules in unit volume and u their velocity. We assume namely that all molecules move equally fast and do not interact with each other. In the dynamical theory of gases it is shown that $\nu = (nu)/4$ molecules strike the unit of surface in unit time, independent of the distribution of the velocities of the molecules and therefore also if all the molecules have the same velocity. Thus $S \cdot (nu)/4$ is the number of molecules which leaves the surface in unit time. Considering that $\bar{\varrho}/u$ represents the mean time between two collisions of a molecule with the surface, it is easily seen that both members of the equation (4) give the number of molecules present in the volume. Simplification of the identical relation (4) gives the theorem (3).

For more-dimensional spaces the proof remains unchanged. Only the formula $\nu = nu/4$ must be replaced by $\nu = nu/\lambda_m$, which can be easily demonstrated.

These considerations are not only much simpler than those of the preceding paragraph but may also be generalised in an easy way. It is namely evident that nothing essential in this proof changes if we consider a number of molecules moving in a spherical surface only. V becomes the area inside a certain closed curve on the sphere, S the total length of this curve and the factor 4 is to be replaced by π, in agreement with formula (1) for a 2-dimensional (be it curved) space.

In this case however the formula is limited in the way that no great circles of the sphere (the orbits of the molecules) may be situated inside the curve in question. This is a consequence of equation (4), which expresses that the molecules present inside V must come from the wall S. Moving about inside V must be impossible.

§ 3. Finally we point out that our theorem still holds in all linear and spherical spaces if we suppose the sets of straight lines and great circles (the tracks of the molecules) replaced by sets of curves of a different shape, of course with the limitation mentioned at the end of § 2.

Hence, with the aid of (1), we find for the mean length of a helix inside a sphere

$$\bar{\varrho}_3 = \frac{4 \cdot \frac{4}{3} \pi R^3}{4 \pi R^2} = \frac{4}{3} R$$

In calculating this mean value we must in the first place consider that an equal number of helices goes out in every direction (in a little elementary solid angle), but in the second place that the planes of osculation of these helices are distributed in a regular way about this direction. If the curve is not movable in itself as the helix we must divide the curve in elements of equal length and take the mean value of ϱ for all the possible positions of the curve. Proceeding in this way

we apply the only method which agrees with a really random distribution of curved lines in a space.

We were not yet able to give an analogical proof as in § 1 of the theorem in its full generality, without the time as a parameter, as in § 2.

In the accessible literature [1]) we have only found some very special cases of the general theorem.

Eindhoven, 8 September 1927. *Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken.*

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[1]) M. W. CROFTON: Phil. Trans. Roy. Soc. Lond., **158**, blz. 181 (1868).
E. CZUBER: Geometrische Wahrscheinlichkeiten, blz. 213 (Leipzig, 1884); Wahrscheinlichkeitsrechnung, erster Band, blz. 115 (Leipzig, 1914).
R. DELTHEIL: Probabilités géométriques, blz. 84 (Paris, 1926).

Applied Geology. — *Earth movements, caused by coalmining.* By J. VERSLUYS.

(Communicated at the meeting of September 24, 1927).

Owing to the removal of coal by mining, a void is created and the equilibrium of the strata at a great depth becomes disturbed. As a result subsidences occur, that are observable even upon the surface.

While the coal is being removed, the roof is firstly propped up with timber, those props, however, are only able to withstand the pressure for a short time and they soon succumb. Nor is the erection of these props intended for the purpose of enduring permanent support. Often the space is left quite open, in many cases, however, this is filled up with lumps of stone. This filling in is seldom complete and the lumps are not firm enough to offer full resistance to the pressure of the strata resting thereon. They become crushed and occupy a smaller space. After a number of years the space occupied by the crushed filling material, is seldom more than 60 % of that occupied previously by the coal removed. Often the volume of the compressed mass is still smaller.

Formerly various opinions prevailed concerning the origin of the subsidences as a consequence of mining operations. An old view was that above the space, occupied previously by the coal, the rock had crumbled, so that the blocks fall and owing to this a natural filling would arise, in so far as the crumbled rock occupies more space than formerly. Consequently crumbling would only go on to a limited height, proportional to the thickness of the coal bed. In that case nothing would be observed on the surface, provided the depth of the coal bed was great enough.

As against this view was another, much older one, namely that the series of beds lying over the area from which coal had been removed, subsided altogether, hence fractures arose at the extremes of the field, perpendicular to the strata. In the case of fig. 1, where *AB* represents the space from which coal has been removed, the mass *ABDE*, would slip along the lines *BD* and *AE*, and subside. Regarding these older theories reference is made to the works of J. GONOT (1), G. DUMONT (2) and a report by the "Union Des Charbonnages" of Liége (3).

These theories have become obsolete as have also the variations of those theories, and the assumptions, in which endeavours are made to reconcile both theories.

Afterwards the theory that now almost generally prevails, that of the deflection of beams arose. It is taken that the strata above the space from which coal has been removed, may be considered as beams that are

fixed in at the extremeties and become deflected. For this theory of deflection, reference is made to text books, i.a. to that by A. H. GOLDREICH (10). Further, attention must still be drawn to the researches and theories of L. THIRIART, from whose hand new publications are continually appearing (lately 15).

The prevailing theories will not be further discussed here. In 1928, in all probability, a more extensive special article, with a more complete bibliography, will apear in the Dutch periodical "De Ingenieur".

Here only will be treated a new explanation of the phenomena observed and with this it will be presumed that the most simple case occurs, viz : that the coal bed lies horizontally.

One of the first questions arising is : If the strata covering the carboniferous consist of loose beds, as sand and clay, will those materials then flow? This question can be answered in the negative. In Dutch-Limburg and Belgian-Limburg (Kempen), where considerable covering strata for the greater part, sand, prevail, the phenomena on the surface of earth do not deviate from those which occur near Liége and in the Borinage, where the firm rock is only covered by a few metres of loose material. Where sand is also lying on the surface, clear evidences of gravity and thrust faulting are to be observed, and these, in this case, have much resemblance to the natural faults in sand. On digging a trench for making a road at Heerlen in 1926 an opportunity occurred of seeing a fault in loose beds (13) owing to which comparison was possible.

It must therefore be taken that the subsidence owing to mining, takes place so gradually that the sand does not become running sand (9).

If fig. 1 represents a vertical section of a developed coalfield, and in this

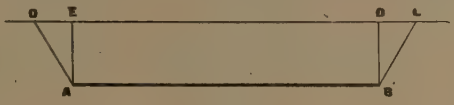

Fig. 1.

the line *AB* represents the part of the coal stratum that has been removed, and *OL* the earth surface, subsidence occurs with a steep incline, about as the lines *AO* and *BL*. A shortening of the surface *ED* is observable, and in the sections *OE* and *DL*, an extension. The influence of the shortening is visible on the buildings, pavement curbs, tramlines, railings, paving stones and such like, owing to compression. Some very remarkable changes of form, which will not be discussed here, are seen. The extensions are similarly observable. What takes place to the left of *O*, and to the right of *L*, in fig. 1, will still further be, at first the conduct of the strata within the trapezium *OABL* will be described.

Previous to a commencement being made with mining operations, the strata overlying the coal rest upon the latter, and there is an equilibrium. This equilibrium is not definite, under varying conditions of stress the mass

can be kept in balance, owing to friction and since a certain force is necessary, to overcome the resistance to tension of the consolidated strata. It is not necessary, though probable, that the vertical stress deviates little from the pressure which a fluid with a specific gravity, equal to that of the beds, would exercise, provided the latter may be considered as being impermeable for water. The horizontal stress may have varying values.

While the coal exerts a certain pressure upwards on the roof, this ceases altogether for a moment, owing to the removal of the coal along the line *AB* in fig. 1. Very soon, however, a pressure that is smaller takes the place of this. This counter pressure is effected by the filling in material, or owing to crushing taking place up to a slight height above the space from which coal has been removed. According to observation this results in the equilibrium being disturbed, real gravity faults occur, at the edges of the field, and horizontal compression and extension, as discussed in the forgoing. As will appear presently the lengthening is to be attributed to gravity faulting, and shortening to thrust faulting. Energy is used up by the crumbling of the filling material, by the formation of fractures in the solid rock and further, by the frictions of the solid parts ; these three kinds of energy are produced by gravity : the mass situated within the trapezium *OABL* in fig. 1, subsides. Within this trapezium sometimes apparent risings are seen on the surface, presumably, however, these are sections that have declined less than the other, owing to thrust faults with smaller heights. A full discussion of the mechanics of deformations in the masses of earth under the influence of the changes in condition of stress can be neglected here. We refer for this to the works of H. KREY (11 and 14). The results of the various tests, i.a. those referred to in the first mentioned work by H. KREY (11) can be applied immediately to what occurs in the trapezium.

In figs. 2 and 3 the rectangles *ABCD* represent the vertical sections of

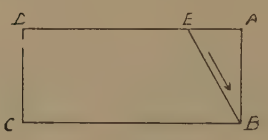

Fig. 2.

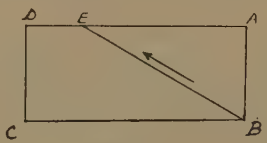

Fig. 3.

receptacles filled with sand, hence *AD* in both the drawings represents the surface of the sand masses, while the end *AB* can be removed parallel to itself. The sand exercises a pressure on the side *AB*. If the pressure from outside, upon this side, be reduced, the mass *ABE* then moves in the direction *BE* in fig. 2, forming an angle with the horizon of about 60°. If however the pressure on *AB* be so much increased that the sand gives way, the mass *ABE* then moves in the direction *BE* in fig. 3, forming an angle with the horizontal of about 30°.

If thus the pressure be reduced in a definite direction, so that movement sets in, then the plane of faulting forms an angle with that direction of about 60°. It may be presumed that owing to the diminishing of the pressure along *AB* in fig. 1 within the rectangle *ABDE*, the vertical stress has become smaller and consequently deformations set in, owing to movement along the planes, forming an angle of 60° with the vertical, or one of 30° with the horizon. This mass thus becomes horizontally compressed and the phenomena occurring within this section, are thrusting faults, and the rectangle *ABDE*, becomes shorter horizontally.

The horizontal pressure on the lines *BD* and *AE* in fig. 1, is reduced, and displacements will take place over a plane having an inclination of about 60°. It would be conceivable that the gravity displacement occurs in two planes *OA* and *BL* in fig. 1, and the thrust in one or two planes. On displacement one plane prevails, there are, however, others and these effect an extension of the surface as appears from fig. 4. In the same manner other displacements effect a contraction.

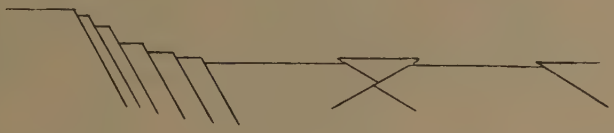

Fig. 4.

PUSCHMANN (5) discusses observations, in a number of tunnels, which had been cut in the coal beds overlying, one or more deeper beds which had already been worked.

From that description it appears that the sandstone strata, overlying the void from which coal had been taken, underwent but slight deformation. The slate appeared to be slightly folded. So the explanation given above holds strictly only for the unconsolidated upper beds, while the carboniferous sandstone and slate show some deviation. The sandstone hardly becomes contracted, above the space from which coal has been removed, and in accordance with this the fracture (*BL* and *OA* in fig. 1) in sandstone beds is practically vertical. Every sediment has its own character and the angle of inclination of the fractures depends upon the nature of the material (12).

Outside of the lines *OA* and *BL* in fig. 1 the ground also moves on account of the mining in the part *AB* of the coalbed. This can be explained according to the same principle as the foregoing. The pressure upon the strata below the line *AB* in fig. 1, declines and thus fractures might arise at a slight angle of inclination. The case, however, is not so simple, and might be better compared with a test that is also described by H. KREY, from which fig. 5 has been taken. A vertical pressure is effected upon a stamp *AB* resting on a mass of sands till the stamp presses the sand away.

The mass then moves as is shown in fig. 5. If the pressure on *AB* is previously already great enough to effect this change of form, this can be prevented by a pressure upon the mass of sand from *A*—*B* and *B*—*D*. If after this the pressure outside the stamp be reduced, the change of form will also set in. In this manner it may be taken that in fig. 1, by reducing the pressure the upward movement along *AB* takes place under a slight inclination, and that the mass to the left of *OA* and right of *BL* declines. In this then faults also occur, and on the surface, to the left of *OA* and the right of *L* some horizontal extension and subsidence may be expected. This is represented in diagram in fig. 6. There is less certainty concerning the inclination of the faulting planes in this region. The movement in the bottom of the coal layer being worked on, is only too well known in the mines and the movement outside of the main fractures in the ground has been observed in shafts, owing to accurate measurements, without this causing any material damage. In fig. 6 left of *O* and to the right of *L* extension must take place on the surface. The sphere of displacement and extension left of *O* in fig. 6, connects up with *AOE* in fig. 1 and left of what is represented in fig. 4. Owing to the succession of strata having different physical characteristics, the situation here will also become changed.

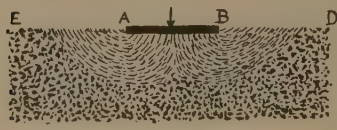

Fig. 5.

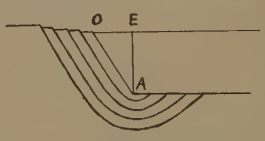

Fig. 6.

With regard to the effect outside of the main planes of fracture, it would appear that in 1899 W. H. TROMPETER (4) held the same view. He speaks of an "expansive force" of the rocks, as the cause of the movement, apparently, however, this writer expressed himself inaccurately and something else is meant by "expansive force". For the rest it is not impossible that clay and soft shale expand, on a reduction of pressure (16). This does not occur in the Limburg coal mines, presumably the rock in this district, at one time, owing to the load of deposits which later disappeared again for a great part owing to erosion, were, under so great a pressure, unable any longer to expand by the absorption of water.

A question of importance with mining is how the shafts can be protected. To protect these completely, as a rule much of the coal around the shafts, has to be sacrified. In this connection it must be pointed out that in one of the mines in Belgium, only a small pillar was left around the shaft, apparently with success, though the formations overlying the carboniferous,

Fig. 7.

for the greater part, consist of sand, having a considerable depth. We then have the situation as in fig. 7. Over the section *MN* the vertical pressure at the top and the bottom of the coalbed, is not directly altered. The displacements will thus avoid this section of the area. The subsidence taking place outside the limits of the field being worked, (outside *AO* and *BL* in fig. 1), as a result will have a decline to a much greater degree at *MNRS* and thus the section *MNRS* will decline, the vertical pressure, however, in *MNRS* will then also decline much less than in the adjoining sections. Hence the section *MNRS* can be compared with the stamp in fig. 5. It must be borne in mind that if in fig. 7 the coal in section *AN* only, be first removed, and only later that of the section *MB*, the main fractures will go through the section *MNRS*, because then the line *MS* may be temporarily compared with the line *AE* in fig. 1. The situation becomes quite otherwise if, as in fig. 7, is presumed, the coal is removed simultaneously from the sections *AN* and *BM*.

If the principles here explained be correct, the great protecting pillars can be worked, provided work be effected as symetrically as possible with respect to the shafts and that near these a narrow strip of coal, perpendicular to the direction in which the coal beds are being worked be left untouched.

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Biochemistry. — *The first phases of the chemistry of the dissimilation of the hexoses.* By A. J. KLUYVER and A. P. STRUYK.

(Communicated at the meeting of June 25, 1927).

§ 1. *Introduction.*

At the meeting of January 30th 1926 a paper by the authors [1]) was presented in which a new scheme — based on the extensive experimental material available — was developed regarding the first phases of the chemistry of the dissimilation of the hexoses.

As the result of the observations regarding the behaviour of the inorganic phosphates by the so-called cell-free fermentation, it was up to that time generally accepted [2]) that the reactions involved in alcoholic fermentation could be represented by the following equations, which were first given by the English investigators HARDEN and YOUNG in 1908:

$$2\,C_6H_{12}O_6 + 2\,PO_4HR_2 = 2\,CO_2 + 2\,C_2H_6O + C_6H_{10}O_4\,(PO_4R_2)_2 \quad (I)$$

$$C_6H_{10}O_4\,(PO_4R_2)_2 + 2\,H_2O = C_6H_{12}O_6 + 2\,PO_4HR_2 \quad (II)$$

It was pointed out by us at that time, how a number of arguments plead in favour of replacing this representation, less satisfactory from a logical point of view, by the following scheme of the process of the splitting up of the hexose:

$$C_6H_{12}O_6 + PO_4R_2H = C_6H_{11}O_5\,(PO_4R_2) + H_2O \quad (I)$$

$$C_6H_{11}O_5\,(PO_4R_2) = C_3H_6O_3 + C_3H_5O_2\,(PO_4R_2) \quad (II)$$

$$C_3H_6O_3 = CO_2 + C_2H_6O \quad (IIIa)$$

$$C_3H_5O_2\,(PO_4R_2) + H_2O = C_3H_6O_3 + PO_4R_2H \quad (III\textit{b})$$

where the $C_3H_6O_3$ produced in equation III*b*, is split up afterwards, also according to III*a*, into carbonic acid and alcohol.

The by-product of the cell-free fermentation of the hexoses, which had been isolated by ROBISON [3]) already four years before, was in this scheme for the first time (however cf. note 2) proclaimed to be the first normal reaction product of the hexoses in fermentative dissimilation.

A further consequence of our view was that the hexose biphosphoric acid, which only appears in case of cell-free fermentation originated from

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[1]) These Proceedings **29**, 322, (1926) and also: Die Naturwissenschaften, Vol. **14**, p. 862 (1926).

[2]) An exception must be made in favour of the American investigator RAYMOND whose publication relating to the matter in question (Proc. Nat. Acad. of Sciences Vol. **11**, p. 622 (1925)) was unknown to us at that time. This very preliminary paper contains, however, practically no documentation, whereas RAYMOND's scheme also deviates from ours in this respect that hexose biphosphate is assumed to be a normally occurring intermediary product.

[3]) R. ROBISON, Biochem. Journ., Vol. **16**, p. 809 (1922).

a carboligatic synthesis of the intermediarily formed triose-monophosphoric ester. Whereas this view as to the origin of the hexose-biphosphoric ester had been given before, a.o. by H. VON EULER [1]), yet our assumption differs fundamentally from the Swedish investigator's view, owing to the fact that the latter only aims at giving a further interpretation of the mutual connection of the equations of HARDEN and YOUNG. In doing so the hexose-biphosphoric ester is accepted as an intermediary product of the normal alcoholic fermentation of the hexoses ; whereas in our fermentation scheme there is no room for this ester and its appearance in case of cell-free fermentations is looked upon by us as an incidental product, in consequence of the breaking-up of the co-ordination of the successive reactions.

We put in view a further experimental test of our assumption, and it was our intention to return to this more in detail in the thesis of one of us (Str.) Various experimental difficulties which presented themselves together with the desirability to pay attention first of all things, in this connection, to the problem (which was in an extremely confused state) of the so-called "co-enzyme" of the alcoholic fermentation [2]), were the cause that the anent investigation was not yet finished.

That we already proceed to publish some of the results obtained by us in this investigation at the present moment, finds its cause in the fact, that from 1926 onward the various hexose-monophosphoric esters, especially the one isolated by ROBISON in 1922, have come to be regarded with the utmost interest by a number of the leading investigators who are occupied with the study of the hexose-dissimilation. We only mention such names as : EMBDEN, MEYERHOF, NEUBERG and VON EULER. We are far from venting the suggestion that this altered situation might be due to the publication of our view, yet it seems desirable to ascertain here, how the exactness of our scheme has derived considerable support from later investigations. As the problem under discussion is now actively and intensively investigated in various laboratories, we thought it advisable not longer to postpone the provisional publication of some of the results obtained by us in this line.

§ 2. *Survey of the more recent investigations which support the hypothesis of the formation of a hexose-monophosphoric ester as the first intermediary product in the dissimilation of the hexoses.*

The first investigator, who, in the course of 1926, declared himself in favour of the supposed formation of a hexose-monophosphoric ester as an intermediary product in the dissimilation of the hexoses, may have been G. EMBDEN. He did so at an oral discussion at the Physiological congress [3])

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[1]) H. VON EULER, Chemie der Enzyme, I Teil, 3e Aufl., p. 336, 1925; Cf. also: Die Naturwissenschaften, Vol. **13**, p. 938 (1925).

[2]) These Proceedings, **30**, 569 (1927).

[3]) O. MEYERHOF, Die Naturwissenschaften, Bd. **14**, p. 1179 (1926).

held at Stockholm in August 1926. In this connection it must be borne in mind, that EMBDEN, in 1917 [1]), announced to have proved that the hexosephosphoric ester, which occurs as the normal precursor of the lactic acid which is produced in the muscular tissue, and to which he had given the name of "Lactacidogen", produces a phenylosazone which is identical with the well-known LEBEDEFF osazone, which is obtained from the hexosebiphosporic ester formed in the case of cell-free alcoholic fermentation. In how far the lactacidogen itself is identical with the above-mentioned ester, was then left undecided. In 1924 [2]), however, EMBDEN arrives at the conclusion: "Hiermit ist der Nachweis erbracht, dasz dem Lactacidogen die Struktur einer Hexosediphosphorsäure zukommt, welche mit der bei der Hefegärung gebildeten Hexosediphosphorsäure vollkommen identisch ist". However, he adds to this that he does not exclude the possibility, that at the same time a hexose-monophosphoric ester also occurs in the muscular tissue. In 1927 there appears the fifth paper on the chemistry of the lactacidogen, in which EMBDEN revokes his former statements to a certain extent [3]). It now has appeared to him that the ester, obtained until that time from the muscular tissue by adding fluoride of sodium, does not occur in the undamaged muscular tissue, but that, on the other hand, it contains a hexose-monophosphoric ester which in fact must be looked upon as the lactacidogen proper. This ester is isolated by him and studied, and he arrives at the conclusion that it is neither identical with NEUBERG's ester, nor with ROBISON's. As regards the latter part of this statement, it seems to us that there is still room left for doubt.

Whereas MEYERHOF until shortly still adhered to the hypothesis on the function of the phosphoric acids in the dissimilation of the hexoses given by HARDEN and YOUNG, as appears from his book "Chemical Dynamics of Life Phaenomena" (finished in April 1924), and even gives new evidence in support of it, he, for the first time, pronounces the opinion of the necessity "einer Umdeutung und Neuformulierung der HARDEN—YOUNG'schen Gärungsgleichungen" in a "Zuschrift" sent to "Die Naturwissenschaften" [4]) on June 30th 1926. As a result of new investigations he has arrived at the following conception of the splitting-up of the hexoses in the muscular-extract: "In der I Periode werden beide Zuckermoleküle phosphoryliert. Das eine Estermolekül zerfällt rasch in statu nascendi was so lange geht, als noch neuer Ester entstehen kann. Das andere Estermolekül stabilisiert sich als Hexosediphosphorsäure". In this publication MEYERHOF leaves as yet undecided the nature of the primarily formed

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[1]) G. EMBDEN und F. LAQUER, Zeitschr. f. physiol. Chemie, Vol. **98**, p. 181 (1917).

[2]) G. EMBDEN und M. ZIMMERMANN. Zeitschr. f. physiol. Chemie, Vol. **141**, p. 225 (1924).

[3]) G. EMBDEN und M. ZIMMERMANN, Zeitschr. f. physiol. Chemie, Vol. **167**, p. 114 (1927).

[4]) O. MEYERHOF, Die Naturwissenschaften, Vol. **14**, p. 756 (1926). Cf. also: Idem, Biochem. Zeitschr., Vol. **178**, p. 462 (1926).

ester. In a paper [1]), published towards the end of 1926, he defines this ester in agreement with EMBDEN's above-mentioned statement, as a labile *mono*phosphoric ester, and gives the following scheme:

$$2\,C_6H_{12}O_6 + 2\,H_3PO_4 = 2\,C_6H_{11}O_5\,(H_2PO_4)^* \text{ (*aktiv)} + 2\,H_2O =$$
$$2\,C_3H_6O_3 + C_6H_{10}O_4\,(H_2PO_4)_2 + 2\,H_2O.$$

Consequently, MEYERHOF too, here comes to the conclusion that a hexose-monophosphoric ester is the first reaction-product in the dissimilation of the hexoses. Starting from this hypothesis MEYERHOF and LOHMANN [2]) have, quite recently, made a detailed investigation to ascertain the behaviour of the various hexose-monophosphoric esters towards muscular-extract and yeast maceration-juice.

In his last summary of the chemistry of the hexosedissimilation (which treatise bears the date of December 1, 1924), NEUBERG [3]) mentions but incidentally the hexose-monophosphoric ester isolated two years before that time by ROBISON, whereas he makes the remark: "seine Bedeutung für den Gärungsvorgang ist noch ungeklärt".

In the same treatise, however, the possibility is left open that, in contradistinction to HARDEN and YOUNG's theory, the formation of hexose-diphosphoric ester "ein unphysiologischer Prozess ist". In a publication [4]) which appeared in 1925, this statement, however, is further developed as follows: "somit ist die *extrazellulare Anhäufung* [5]) von Zucker-phosphorsäure-ester von C. NEUBERG und seinen Mitarbeitern nicht ohne Recht als ein unphysiologischer Prozess bezeichnet". On the other hand, the fact, that the phosphoric ester does not accumulate in the sugar-fermentation by living yeast-cells, is ascribed to the perfect co-ordination of the binding and splitting-off of the phosphate present in these cells. From this it must be inferred that NEUBERG at that time looked upon the hexose-biphosphoric ester as a normal intermediary product of the alcoholic fermentation of the hexoses. In agreement with this the hexose-biphosphoric ester continues to remain the focus of interest in some later publications of NEUBERG and KOBEL [6]).

In a paper [7]) published towards the end of 1926 the following statement strikes us: "In den Vordergrund des Interesses ist nun neuerdings die Hexose-*mono*phosphorsäure gerückt". In connection herewith observations are given on the fermentability of the three different hexose-*mono*phos-

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[1]) O. MEYERHOF, Die Naturwissenschaften, Vol. **14**, p. 1175 (1926).

[2]) O. MEYERHOF und K. LOHMANN, Biochem. Zeitschr., Vol. **185**, p. 113 (1927).

[3]) C. NEUBERG in OPPENHEIMER, Handbuch der Biochemie des Menschen und der Tiere, 2te Aufl., II Vol., p. 453 (1925).

[4]) C. NEUBERG und A. GOTTSCHALK, Biochem. Zeitschr., Vol. **161**, p. 254 (1925).

[5]) NEUBERG himself prints in italics.

[6]) C. NEUBERG und M. KOBEL, Biochem. Zeitschr., Vol. **166**, p. 488 (1925). Ibid. Vol. **174**, p. 480 (1926).

[7]) C. NEUBERG und M. KOBEL, Biochem. Zeitschr., Vol. **179**, p. 451 (1926).

phoric esters. In a very recent publication [1]) the question is moved how far "im Mono-phosphorsäure-ester wirklich das lang gesuchte obligatorische Zwischenprodukt der Gärung vorliegt", and NEUBERG gives here as his opinion that the high yields of ROBISON's ester obtained by him are "vielleicht ein Argument zugunsten der Ansicht, dasz dem Gärungsmonophosphat der Rang eines wichtigen Durchgangsgebildes zukommt".

In 1924 VON EULER and MYRBÄCK [2]) still write: „Durch die hier mitgeteilten Versuche gewinnt die HARDENsche Theorie über die Beteiligung des Hexose-diphosphates als Zwischenprodukt der Gärung eine neue Stütze". Shortly afterwards VON EULER and BRUNIUS [3]) express themselves even more positively, as may appear from the following quotation: "dasz also die Bildung des Hexose Diphosphates $C_6H_{10}O_4\,(PO_4R_2)_2$ eine notwendige einleitende Teilreaktion der alkoholischen Gärung ist, kann nunmehr als feststehend angesehen werden". In a "Zuschrift" to "Die Naturwissenschaften" [4]) which bears the date of the 24th of September 1925, VON EULER expresses himself as follows: "Für die normale alkoholische Gärung können die HARDENschen Gärungsgleichungen als *bewiesen* [5]) gelten". It is true that VON EULER, in writing this, feels the want of giving a more detailed representation of the connection, which, on the strength of these equations, must exist between the fermentation of the first and the esterification of the second hexose-molecule. He therefore develops a conception according to which the chemistry of the hexoses might be represented as follows:

$$C_6H_{12}O_6 + PO_4HR_2 = C_3H_6O_3 + C_3H_5O_2\,(PO_4R_2)$$
$$2\,C_3H_5O_2\,(PO_4R_2) = C_6H_{10}O_4\,(PO_4R_2)_2$$

VON EULER imagines that the reacting glucose molecule is first split up into two molecules, each containing 3 C atoms, the former of which is afterwards esterified with phosphate, whereas the latter is fermented into alcohol and carbonic acid. Further, the synthesis of the hexose-biphosphate it said to take place "auf Kosten der energieärmeren, vergärenden Glukosehälfte". Without entering into a more direct consideration of this assumption, we only want to point out here, that it only tallies in one respect with our scheme, viz. as regards the formation of the hexose-biphosphate from two molecules of triosephosphate. For the rest it is altogether different from it. For, according to VON EULER the fermentation is made subservient to the synthesis of the hexose-bi-phosphate, whereas the main point of our conception lies in the fact that the phosphorylation of a hexose molecule is made subservient to the splitting up of the same molecule. Moreover according to VON EULER it is the triosemolecule which is

[1]) C. NEUBERG und J. LEIBOWITZ, Biochem. Zeitschr., Vol. **184**, p. 489 (1927).

[2]) H. VON EULER und K. MYRBÄCK, Zeitschr. f. physiol. Chemie, Vol. **139**, p. 15. (1924).

[3]) H. VON EULER und E. BRUNIUS, Svensk Kemisk Tidskrift, Vol. **37**, p. 301 (1925).

[4]) H. VON EULER, Die Naturwissenschaften, Vol. **13**, p. 938 (1925).

[5]) We print in italics.

esterified, whereas, in our conception, it is the esterification of the glucose-molecule, i.e. the formation of the hexose-mono-phosphate that comes to the fore. In a recent paper, however, VON EULER [1]) also hints at the possibility of the hexose-monophosphate playing a part in the first splitting-up to which the hexosemolecule is subjected in the dissimilation.

§ 3. *Personal observations on the appearance of hexose-monophosphoric ester in the cell-free fermentation.*

As it has already been stated, the consideration which induced us to publish our experiments, though incomplete, was the fact that some weeks ago an extensive communication was published by NEUBERG and LEIBOWITZ (l.c.), which contains numerous data regarding the coming to the front of hexose-monophosphoric ester when maceration-extract reacts on hexoses in presence of inorganic phosphates.

In connection with what follows it may be pointed out, that these investigators give no explanation whatever of this remarkable fact, which differs from the results obtained by former investigators, and derive no conclusion whatever from their experiments, with the exception of the above-quoted guarded statement given in a footnote.

As regards our own observations, which partly date from the latter half of 1926, the following introductory remarks may be made.

The scheme made up by us, naturally includes that the hexose-biphosphoric ester can only be formed, if, by the side of the phosphatese, the oxydoreducing agent of the yeast, the zymase in the narrower sense, can also come into action. This agent is both indespensable for the splitting-up of the hexose-monophosphoric ester, and the carboligatic synthesis of the triose-*mono*phosphoric ester formed. The most beautiful demonstration of the exactness of our view would have been a separation of the phosphorylating from the oxydoreducing agent of the yeast, for, in that case, the esterified phosphate ought to have been found back exclusively as hexose-*mono*phosphoric ester. A similar isolation of the phosphorylating agent has been tried more than once, and as far as we know a positive result has been reported but only once.

In 1912 EULER and OHLSÉN [2]) state that an extract of a special kind of yeast brings about esterification under very special circumstances, without producing carbonic acid. A further investigation of the ester formed has, however, not taken place. A repetition of the said experiment, with the yeast-species that were at our disposal, yielded, however, a negative result, in accordance with the experience other investigators had obtained on this point. Starting from the fact that fluoride of sodium in the muscular tissue, does not interfere with the phosphorylation, but stops the formation of

[1]) H. VON EULER und K. MYRBÄCK, Zeitschr. f. physiol. Chemie, Vol. **165**, p. 44, (1927).

[2]) H. VON EULER und HJ. OLSÉN, Zeitschr. f. physiol. Chemie. Vol. **76**, p. 468 (1912).

lactic acid, it was now tried, by adding this salt to produce a similar effect in case of the reaction of maceration extract on hexoses.

Experiments made with various concentrations of Na F showed that neither in this way a separation of the two functions could be brought about. Neither esterification nor fermentation took place with the higher concentrations, and as soon as the esterification did set in when the concentration of the poison was reduced, carbonic acid was always formed at the same time. Incidentally it may be stated that after that time MEYERHOF [1]) has also come to the same result.

Attempts to come to a phosphorylation with a total absence of fermentation in the reaction of zymase-preparations and hexoses, had to be given up for the present. Meanwhile, attempts aiming at isolating the triosephosphate which IWANOFF found at one time in the fermentation medium, had drawn our attention to the great differences which manifested themselves in the nature of the rate of fermentation in presence of inorganic phosphates, when different maceration juices were used. It was tempting to trace to what extent this divergent behaviour manifested itself also in the nature of the hexosephosphoric esters appearing in the fermentation media.

It may be stated at once that this appeared to be the case.

We subjoin the result of two typical experiments which, however, are only instances of a series of observations which yielded similar results.

In order to prevent misunderstanding, it may be stated that the yeast used for the preparation of the maceration juice was the same yeast in all these experiments, viz. bottom-yeast of the d' Oranjeboom Brewery at Rotterdam [2]). Meanwhile it has appeared to us from other experiments, that the properties of the maceration juices prepared from this yeast, vary a good deal, according to the previous history of the yeast which is worked up, and according to the duration of the operations to which the dry yeast was subjected before the maceration.

Two typical instances are given below of the progress of the production of carbonic acid in the fermentation of glucose, in the presence of inorganic phosphates, with the aid of maceration-juices prepared from two different portions of dried yeast.

With these experiments 5 grams of glucose were brought to fermentation with 25 cc. of the maceration-juice which were kept shaking in a thermostate at 30° C.

When the rate of fermentation had become constant, 25 cc. of a 6 % solution of one part of NaH_2PO_4 and five parts of Na_2HPO_4 were added.

The two curves *A* and *B* of Figure 1 mark the progress observed of the rate of fermentation, i.e. the quantity of carbonic acid liberated every 5 minutes. Whereas with the aid of the maceration-juice obtained from

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[1]) O. MEYERHOF, Biochem. Zeitschr.. Vol. **183**, p. 176 (1927).

[2]) We herewith express our heartfelt thanks towards the directors and the bacteriologist of this brewery for the readiness with which they have always put yeast at our disposal.

yeast-sample *A*, a progress of carbonic-acid development is obtained which is characterised by the rapid reaching of the maximum and a subsequent,

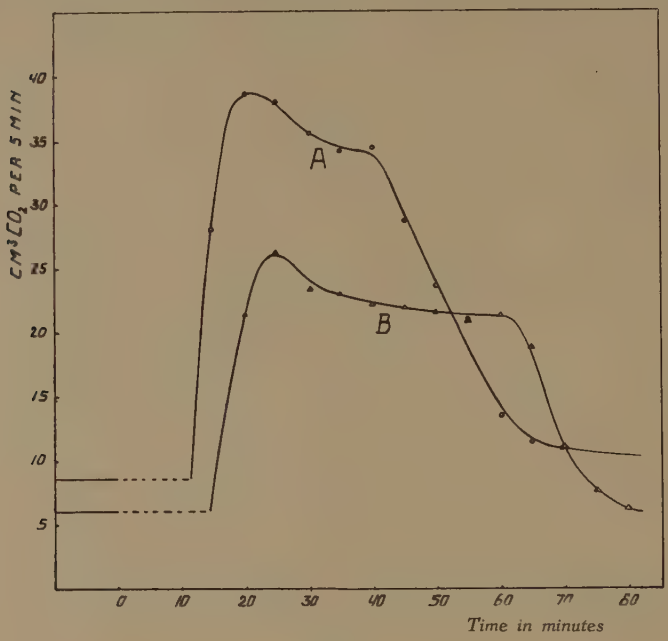

Fig. 1.

constant decrease in the rate of fermentation, it is seen that the addition of phosphate to the maceration-juice prepared from yeast-sample *B* has a different influence. The increase in rate of fermentation is considerably less in this case, but on the other hand, the increase in velocity continues to exist for a longer time. After complete esterification had set in, which, at the same time, revealed itself by the fact that the rate of fermentation fell back to its original value, we proceeded, in both cases, to a further investigation of the phosphoric esters present at than point of time. In doing so, the method of separation (elaborated by ROBISON [1]) of the hexose-*mono*-phosphoric and hexose-*bi*phosphoric esters with the aid of the Ba-salts, was applied. For this purpose the yeast-mixture was first slightly acidified towards litmus, and afterwards poured out into half a volume of boiling water, to stop the enzyme-action spontaneously. After having boiled this for a short moment, the liquid was sucked off from the protein precipitated while still hot, and the precipitate was washed with hot water. The required quantity of solid acetate of barium was added to the combined filtrates and the liquid was neutralised with baryta towards phenolphta-

[1]) l. c.

leine. Independent of the appearance or non-appearance of a precipitate with these operations, one or two volumes of 96 % alcohol were added to the liquid. Owing to this the Ba-salts of the various hexose-phosphoric esters precipitate almost completely.

This precipitate was brought over on a Buchner-funnel and after removing the liquid, it was washed with 70 % alcohol, and afterwards treated for one night with boiling absolute alcohol to denaturalise the protein present, if any. The dried precipitate was weighed, and then extracted with the tenfold weight of cold water ; which brings about the solution of the Ba-salts of the hexose-*mono*phosphoric ester, whereas nearly the whole of the much less soluble Ba-salt of the hexose-*bi*phosphoric ester remains behind.

The Ba-salts of the esters prepared with the *A*-yeast and *B*-yeast show a very striking difference in the above-mentioned treatment, as appears from the following figures :

	A-yeast	*B*-yeast
Weight of the *Ba*-salts	4.055 gr.	4.050 gr.
„ „ „ „ after extraction with 40 cc. of water and subsequent drying	1.810 gr.	traces

Although not the whole of the dissolved substance may be looked upon as the Ba-salt of the mono-ester, yet it may be concluded with certainty from the behaviour of the esters obtained by *B*-yeast, that only a very small quantity of hexose-biphosphoric ester was present in them. That indeed the phosphate, when the fermentation was stopped, was present as a hexose-*mono*phosphoric ester, was further proven by a purification of the Ba-salts which had been dissolved (by a conversion via the lead salt) and the preparation of the phenylosazone of the liberated acid. This osazone had, in accordance with ROBISON's statement, a melting-point of 139—141° C. In contradistinction to this, a hexose-phosphoric acid could be prepared from the remaining Ba-salts of the esters prepared with *A*-yeast by applying the usual purification-methods, which produced a phenylosazone which agreed in every respect with the wellknown LEBEDEFF-osazone (melting-point 151°).

These experiments were repeated a number of times and it appeared that special yeast-samples always behaved in accordance with the *B*-samples. In all these cases the relation of the hexose-monophosphoric ester to the hexose-biphosphoric ester appeared to have been altogether shifted to the first, this being contrary to ROBISON's experience and the experience obtained with other yeast-samples. Owing to these results it had been ascertained that, under the conditions chosen for special yeast-samples, the

hexose-monophosphoric ester might, from a relatively unimportant secondary product of the dissimilation, become the main-product.

How are we to explain the differences in the behaviour of the various maceration-extracts described above? In the light of the conception, advocated by us, of the catalytic agents active in the alcoholic fermentation of the hexoses, the following view seems satisfactory to us in every respect. Whereas it is usual to assume that the various successive reactions which take place in the fermentation proceed each under the influence of a specific catalyst, we place ourselves on the point that only two agents are active, viz:

a. an esterifying agent, which is also able to split up the esters [1]).

b. an oxydoreducing agent.

Whereas in the living yeast cell both catalysts are present in a harmonious quantity, so that the different reactions of our scheme take place in succession, this situation is changed if it is tried to withdraw from the cell the active agents by preparing maceration-juices. In the normal maceration-juices, which among other things show the course of fermentation described by HARDEN and YOUNG, the first-mentioned agent has evidently been weakened in proportion to the second. This appears from the fact that the hydrolysis of the triosephosphoric ester formed has been weakened, owing to which the latter, under the influence of the abundantly present oxydoreducing agent, condenses to hexose-biphosphoric ester. It appears to us, that the phenomena observed with the abnormal maceration-juices described above, find an unconstrained explanation, if we assume that in these juices the relation of the phosphatese (-ase) and the oxydoreducing-agent has been shifted in favour of the first-mentioned agent. For, to be sure, then an accumulation of the triose-phosphoric ester which leads to the formation of hexose-biphosphoric ester will not take place, but it may be expected on the other hand that the first reaction incited by the oxydoreducing agent, i.e. the splitting-up of the hexose-monophosphoric ester, will fall behind to the production of the last-mentioned substance. So accumulation of this substance shall take place, which is in accordance with the facts observed. In accordance with the conception that the zymase function proper has relatively been weakened a great deal in case of the maceration juices prepared from our "abnormal" sample of yeast, there is also the fact that these extracts do not lend themselves to the co-enzyme experiments described in a former paper by us, because they are soon irreversibly inactivated on continued washing.

On the ground of the view developed above, the maceration-juices (which behave according to HARDEN and YOUNG's description) may with the same right be called "abnormal" as the maceration-juices with different

[1]) We leave open the possibility, that it would be desirable to assume the existence of a separate phosphatese and phosphatase, like VON EULER does. The undermentioned considerations become a little more complicated, owing to this, but need not be materially changed.

behaviour, and in the fitness of our scheme to explain these divergent phenomena, we find further indication in favour of its correctness.

§ 4. *The appearance of the triose-stage in the cell-free fermentation of the hexoses.*

Another point, by which experimental support might be given to the scheme proposed by us, would be the isolation of the triose-monophosphoric ester assumed by us as an intermediary product. As is known, L. IWANOFF reports as early as in 1907, so at the very beginning of the examination of the biochemical phosphorylation, the isolation of such an ester. Later investigators however, have never been able to confirm this result, with the exception of the fact that EULER and FODOR [1]) in 1911, make mention of this ester by the side of the hexose-biphosphoric ester. In our first paper on this subject we already pointed out that the different results of IWANOFF and the later investigators might be the consequence of the use of different phosphate concentrations in the esterification, and therefore we made up our mind to repeat the experiments strictly in accordance with IWANOFF's prescriptions. In spite of various attempts we have not succeeded in isolating the osazone described by IWANOFF, although we not only applied the not very clear prescription by IWANOFF but made as well manyfold variations in the way of isolation of the triosephosphoric ester.

The negative result of these experiments made us consider whether the presence of triosephosphoric ester in the fermentation-medium, after esterification had set in, might not be ascertained by other means. In doing so we made use of the triose reaction given by NEUBERG and co-operators [2]). These investigators were able to ascertain that various trioses and also dioxyacetonephosphoric ester — in case of distillation with sulphuric acid and keeping the volume constant by addition of water — are converted to a very important degree into methylglyoxal volatile with steam. The latter substance can then be demonstrated in the distillate as p-nitrophenylosazone and hereupon a quantitative estimation, at least as regards the free trioses, can be established.

It appeared to us that 10 cc. of a yeast mixture, according to IWANOFF's receipt (40 grams of zymin, 50 grams of glucose, 10 grams of Na_2HPO_4 12 aq. in 1000 cc. of water) after a three-days' fermentation at room-temperature distilled in the above-mentioned way, produced with p-nitrophenylosazone a compact precipitate of the methylglyoxal-p-nitrophenylosazone. We had already settled before in accordance with NEUBERG that the reaction turns out practically negative with the various hexoses, and also with hexose-biphosphoric ester. The same could also be ascertained as regards ROBISON's mono-ester. A special blank-test, moreover, showed

[1]) H. VON EULER und A. FODOR, Biochem. Zeitschr., Bd. 36, pag. 401 (1911).

[2]) C. NEUBERG, E. FÄRBER, A. LEVITE und E. SCHWENK, Biochem. Zeitschr., Vol. 83, p. 244 (1917).

us that a mixture of the said quantities of phosphate, glucose and zymin killed by boiling only gave a negligible triose reaction in the period of time under consideration [1]).

It seemed to us a matter of importance to ascertain how far the triose-reaction observed, was based on the appearance of free triose or rather of a triose-phosphoric ester in the fermentation medium. For this purpose the zymin of a second similar experiment was removed after two days by centrifugation. In the clear solution which we obtained, in which hardly any inorganic phosphate could be found, the quantity of triose was estimated by weighing the quantity of osazone obtained. After this it was slightly acidified with acetic acid, boiled a minute and removed by filtration from the protein coagulated. The precipitate was washed and the filtrates were at a low temperature evaporated to one seventh of the original volume in the Faust-Heim apparatus. Another triose-estimation was made in these concentrated filtrates. Thereupon the Ba-salts of the phosphoric esters were precipitated in the way described above and the triose was estimated once again both in the precipitate and in the filtrate.

The following quantities of osazone were isolated in this experiment (calculated for the entire quantity of centrifugate (200 cc.)) :

In the untreated liquid . . . . . 620 mgr.
After boiling and concentration . . 425 „
In the Ba-precipitate . . . . . traces
In the filtrate of the Ba-precipitate . 430 mgr.

From these experiments it appears in the first place that part of the triose when concentration is applied disappears, either by volatilization or by conversion. Although the entire quantity of triose present at the outset (about 150 mgr.) must be called rather small as regards the quantity of the glucose used, this quantity is not so small, however, as regards the quantity of esterified phosphate (about 800 mgr. of anhydrous Na_2HPO_4).

However, the negative result of the triose-reaction in the precipitated Ba-salts, does not make it probable that a triose-phosphoric ester should be present. As, however, the possibility did not seem to be excluded, that the Ba-salt of a similar ester would be soluble in water relatively well, the experiment was once more repeated while the phosphorus was simultaneously estimated. This was done according to the well-known method of NEUMANN, and as regards the small quantities according to the calorimetric method of MARTLAND and ROBISON [2]).

The following results (also calculated for 200 cc. of centrifugate), were now obtained. (See next page.)

From these figures it is shown conclusively, that by far the greater part of the triose is found in the filtrate last mentioned, and certainly is not present in it as phosphoric ester. Moreover, it appears from the fact that the

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[1]) H. A. SPOEHR and P. C. WILBUR, Journal of Biol. Chem., Vol. **69**, p. 421 (1926).
[2]) M. MARTLAND and R. ROBISON, Biochem. Journ., Vol. **20**, pag. 847 (1926).

	Osazone in milligrams	*P* inorganic in milligr.	*P* bound in milligr.
In the untreated liquid	560	9.0	
After boiling and concentration . .	362	15.0	275
In the *Ba*-precipitate	40	—	269
In the filtrate of the *Ba*-precipitate .	335	—	9

quantity of free phosphate remains practically constant in boiling and concentration, that no splitting-up of a triosephosphoric ester, of which the presence at the outset might be deemed possible, occurs.

As in the case of the first experiment the phenomenon, however, appears that the triose-quantity is reduced to about two thirds in the evaporation of the solution. Whereas tests to check this showed that glycerine aldehyde does not disappear when exposed to our procedure of boiling and evaporation, there yet remains the possibility, that this decrease of the triose-reaction is a consequence of the condensation of an eventually present triosephosphoric ester. This possibility is further being investigated at present. Although a small quantity of the triose was found again in the Ba-precipitate on this occasion, this quantity is too small to attach any importance to it as yet.

The experiments were now continued in order to ascertain how far indications of the appearance of triose might be obtained in the case of esterification during a short time with the aid of maceration-juice, and by using a higher concentration of phosphate. It seemed plausible to us, that, immediately after the end of a typical "phosphate-period", a certain amount of triose-phosphoric ester would be present. We shall not enter into details of this series of experiments which have not yet been finished. It may only be stated here that, in using certain maceration-juices, very convincing triose-reactions, were again obtained. In using other maceration-juices, however, no or only weak reactions were met with. The most important thing in this, however, was, that those very juices which show a typical "phosphate-period" (as described by HARDEN and YOUNG), gave a strong reaction, whereas those extracts, of which it has been stated in the preceding section that they produce much hexose-*mono*phosphoric ester, developed no reaction at all or but a very weak one. Experiments to ascertain whether the substance, which develops the triose reaction can be precipitated by direct preparation of the lead salts, yielded no positive result up till this time.

Summarizing all this, the conclusion must be drawn that we have not yet succeeded to prove the formation of a triosephosphoric ester in the dissimilation of the hexoses. That great difficulties will be connected with this follows from our scheme at first sight, as this ester is subject to two kinds of conversions; viz. a hydrolysis on the one hand and a condensation on

the other, so that here a weakening of one of the two catalytic agents does not lead to an accumulation, as is the case with the other intermediary products.

Nevertheless the results obtained did not seem to us to be altogether without importance, as practically no observations of the triose stage in the alcoholic fermentation of the sugars had been made with positive results [1]). NEUBERG still writes in his summary in OPPENHEIMER's Handbuch der Biochemie, which has been quoted already before: "Wie mehrfach erwähnt worden ist, ist das intermediaire Auftreten von Triosen beim Gärungsprozesse noch nicht bewiesen" [2]). In this respect, the investigations described above, seem to fill up a void and, at the same time, they support the scheme drawn up by us.

Delft, June 1927.

From the Laboratory for Microbiology of the Technical University of Delft.

[1]) The old investigation of P. BOYSEN-JENSEN, Biochem. Zeitschr., Vol. 58, p. 451 (1914), is very little convincing in this respect.

[2]) l. c., p. 458.

Chemistry. — *Investigations into the Structure of the Artificial Ultramarines.* **III.** *On Silver- and Alcali-silver-Ultramarines which are Derivatives of* GUIMET's *Ultramarine-blue with high Silica-content, and on Mixed Alcali-Ultramarines and norm. Butyl-silver-Ultramarine.* By Prof. Dr. F. M. JAEGER and Mr. F. A. VAN MELLE.

(Communicated at the meeting of September 24, 1927).

§ 1. A short time ago we published some data [1]) obtained by means of X-rays in the study of GUIMET's *ultramarine-blue* with high silica-content N°. 7553, and of the *silver*-compounds prepared from it. The original *ultramarine-blue* gave, on complete analysis: 15.40 % *Na*; 13.0 % *Al*; 19.20 % *Si*; 10.6 % *S* and 41.8 % *O*. On treatment with very diluted hydrochloric acid, in the way indicated by HEUMANN [2]), we determined afterwards the so-called „clay-residue": this appeared to be 2.78 % of the total mass investigated and contained: 35.6 % *Si* (= 75.8 % SiO_2), 24 % Fe_2O_3 + a little Al_2O_3, and traces only (about 0.9 %) of alcali-oxydes. If these numbers be taken into account, the composition of the *pure ultramarine-blue* is expressed by: 15.63 % *Na*; 12.81 % *Al*; 18.65 % *Si*; 10.90 % *S* and 42.01 % *O*. The composition of pure GUIMET's *ultramarine-blue*, therefore, approaches very near to one expressed by the formula: $Na_6Al_4Si_6O_{23}S_3$, which postulates: 15.73 % *Na*; 12.30 % *Al*; 19.27 % *Si*; 10.92 % *S* and 41.78 % *O*. The number of oxygen-atoms remains uncertain, because in its percentage-number all experimental errors of the analysis of the other elements are accumulated. As is always the case, there is also here too much *Al* and a slight excess of *S*. If this fact be taken into account, the formula of pure *ultramarine-blue* might also be written as: $Na_6Al_4Si_6O_{24}S_3$, which postulates: 15.45 % *Na*; 12.08 % *Al*; 18.93 % *Si*; 10.71 % *S* and 42.83 % *O*. The last mentioned formula should even be preferred in connection with the crystallographical symmetry of this compound. In the following pages we have, therefore, adopted it, although this choice remains arbitrary with respect to the analysis *alone*; it is impossible to decide about the truth of one of these two formulae.

In connection with the constitution of this GUIMET's *blue* N°. 7553, we have in our last publication attributed an analogous constitution to the

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[1]) F. M. JAEGER, H. G. K. WESTENBRINK and F. A. VAN MELLE, Proceed. R. Acad. of Sciences Amsterdam, **30**, 249, (1927); F. M. JAEGER and F. A. VAN MELLE, ibidem, **30**, 479, (1927).

[2]) K. HEUMANN, Lieb. Ann. d. Chemie, **199**, 253, (1879).

Ag-compounds derived from it, guided there-in by the *Ag*-content determined in each case. But on closer examination the *Ag*-content of the *silver-ultramarine* did not appear to be always the same, varying between 41 % and 47 %. Moreover, it was stated that *silver*-compounds with higher *Ag*-content have also always admixed a little more of Ag_2S, than those with lower *Ag*-content : the Ag_2S, as became clear, can never be completely removed, not even by means of repeated decantations. Moreover, a more detailed examination of the reaction-products originated by the action of concentrated solution of $AgNO_3$ at 120° or 130° C. on GUIMET's *blue*, caused us to study the quantitative side of the process, as well as to determine accurately the constitution of the final product by complete analysis of it.

When the sealed glass-tubes, in which the reaction took place, were opened, the presence could always be stated of gaseous products, consisting of oxydes of nitrogen, and principally of NO_2, besides traces of H_2S. From the solution, moreover, we were able to separate in each case: $NaNO_3$, traces of Ag_2SO_4, an appreciable amount of SiO_2, Ag_2O and Ag_2S, besides little quantities of *Ag*, Al_2O_3 and free *sulphur*. These facts prove the interaction of the *silvernitrate* and the *ultramarine-blue* to be under these circumstances of a much more thorough nature, than a simple substitution of *Na* by *Ag* beforehand might suggest.

The finely divided *Ag*, the Ag_2O and the Ag_2S were removed as completely as possible, on treatment of the *Ag-ultramarine* by solutions of *iodine* in *potassium-iodide* and of *potassium-cyanide* (20 %), in the way formerly described, and by repeated decantations. After a 4 times repeated decantation of the thus obtained product, finally a first fraction of lowest specific weight was obtained, which appeared to differ from the remaining part by its complete lack of *iron-oxyde* as an impurity ; its *Ag*-content was only 41 %. The remaining fractions representing by far the principal bulk of the product, appeared all to have an *Ag*-content of 43.9 % or 44 %. Both fractions were completely analysed and gave the following results :

A. Analysis of the first fraction, iron-free, of Silver-ultramarine : 41.17 % *Ag* ; 1.10 % *Na* ; 10.90 % *Si* ; 10.45 % *Al* ; 6.79 % *S* and 29.59 % *O*. If the small amount of *Na*, together with the slight excess of *S*. be considered as an impurity admixed, the composition of this fraction appears to approach very closely to that of a compound : $Ag_6Al_6Si_6O_{29}S_3$, — which formula would correspond to : 42.0 % *Ag* ; 11.0 % *Si* ; 10.6 % *Al* ; 6.25 % *S* and 30.1 % *O* ; the number for *O* being the most uncertain here also for the same reason as formerly indicated.

B. Analysis of the principal mass of the Silver-ultramarine obtained : 43.90 % *Ag* ; 1.21 % *Na* ; 10.85 % *Si* ; 10.45 % *Al* ; 6.80 % *S* and 26.80 % *O*. If also in this case an amount of 1.75 % Ag_2S (estimated by means of the microscope) admixed, be subtracted and the small quantity of *Na* with a trace of the *S* be considered as an impurity, the composition of the principal mass of the product obtained evidently appears to approach

very closely to a compound of the formula: $Ag_6Al_6Si_6O_{28}S_3$, — which formula would require: 42.5 % *Ag*; 11.2 % *Si*; 10.7 % *Al*; 6.32 % *S* and 29.5 % *O*. Also in this case no definite choice can be made between both formulae, because of the uncertainty of the percentage of *O* and the incomplete homogeneity of the products. But it is now perfectly certain, that the *Ag-ultramarine* formed does *no* longer contain 4 atoms of *Al*, as the original GUIMET's *blue*, but 6 atoms of *Al*. If in this case also, because of the identical symmetries of *Ag-* and *Na-ultramarine*, the formula with an *even* number of *O*-atoms be preferred, then the formula: $Ag_6Al_6Si_6O_{28}S_3$ or $Ag_6Al_6Si_6O_{30}S_3$, must probably be attributed [1]) to the pure product. As for the production of this compound *at least* 2 molecules of GUIMET's *blue* must have been used in the reaction, it now becomes clear that the interaction of the original *ultramarine* with the solution of *silvernitrate* in sealed tubes at 120° or 130° C., must necessarily be accompanied by a liberation of SiO_2, Al_2O_3 and *S*. In this process the nitric acid which, by hydrolysis, is set free under these circumstances from the nitrate, undoubtedly plays an important part, as it will immediately react with the GUIMET's *blue*, — which is highly sensitive to the action of acids present, — in causing the production [2]) of H_2S and free *S*. If all possibilities be taken into account, the total reaction might schematically be represented by one of the two following equations:

$$26\ Na_6Al_4Si_6O_{24}S_3 + 156\ AgNO_3 + nH_2O = 156\ NaNO_3 + 24\ Ag_2S + \\ + 9\ Ag_2O + 12\ Ag_2SO_4 + nH_2O + 90\ SiO_2 + 19\ Al_2O_3 + \\ + 9\ S + 11\ Ag_6Al_6Si_6O_{30}S_3;$$

or:

$$52\ Na_6Al_4Si_6O_{24}S_3 + 312\ AgNO_3 + nH_2O = 312\ NaNO_3 + 37\ Ag_2S + \\ + 18\ Ag_2O + 35\ Ag_2SO_4 + 180\ SiO_2 + 38\ Al_2O_3 + 18\ S + \\ + nH_2O + 22\ Ag_6Al_6Si_6O_{28}S_3.$$

If the temperature remains rather low, e.g. 100° or 110° C., the quantity of *S* set free is only small and neither is an appreciable formation of Ag_2O observed in that case. The reaction might then perhaps be described by one of the two more simple formulae:

$$8\ Na_6Al_4Si_6O_{24}S_3 + 48\ AgNO_3 + nH_2O = 4\ Ag_6Al_6Si_6O_{30}S_3 + 24SiO_2 + \\ + 4\ Al_2O_3 + 48\ NaNO_3 + 3\ Ag_2SO_4 + 9\ Ag_2S + nH_2O;$$

or:

$$8\ Na_6Al_4Si_6O_{24}S_3 + 48\ AgNO_3 + nH_2O = 4\ Ag_6Al_6Si_6O_{28}S_3 + 24\ SiO_2 + \\ + 4\ Al_2O_3 + 48\ NaNO_3 + 5\ Ag_2SO_4 + 7\ Ag_2S + nH_2O,$$

Although the same quantity of *water* is found before and after the experi-

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[1]) The formula: $Ag_6Al_6Si_6O_{30}S_3$ requires: 41.60 % *Ag*; 10.45 % *Al*; 10.91 % *Si*; 6.18 % *S*; and 30.85 % *O*. The watery extract of GUIMET's blue does not give a reaction with *Ba*-salts, indicating any presence of *sulphates*.

[2]) Diluted acids, on reacting with GUIMET's *blue*, cause $^3/_4$ of the sulphur present to be precipitated as free *S*, while $^1/_4$ is changed into H_2S. In the above equations this fact is taken into consideration.

ment, it is notwithstanding that written down in the equations, because of its playing a predominant part in the whole series of events during the reaction.

§ 2. The conclusions drawn in our previous paper are *not* changed in their principal outlines by the new interpretation of the reactions mentioned above. It must only be kept in mind that the constitution of *some* of the preparations there investigated will probably be different from what has been indicated. More particularly this will be the case for preparation 19^{II}, which was obtained from *Na-ultramarine* by prolongated heating with an ammoniacal solution of $AgCl$, and which had a content of 31.6 % Ag; this substance might, indeed, perhaps correspond almost completely to a *silverultramarine*, in which $^2/_3$ of the Na of the original GUIMET's *blue* is substituted by Ag, therefore possessing in that case a formula: $Ag_4Na_2Al_6Si_6O_{28}S_3$ or $Ag_4Na_2Al_6Si_6O_{30}S_3$; the first formula requires: 31.85 % Ag, the last one: 31.14 % Ag. But because of the fact, that in the solution of $AgCl$ used, there could not be found, — even after heating for a long time, — any appreciable amount of Al_2O_3 or SiO_2, it is not improbable that finally the preparations 19^I and 19^{II} of the previous paper should yet prove to be derivatives of a silicate with only 4 Al-atoms. On the contrary, the products N°. 4 and 9 obtained from *silver-ultramarine* by melting with NaI or by boiling it with a solution of $NaCl$, must surely be considered as derivative with 6 atoms of Al pro molecule. This difference in constitution must, therefore, necessarily be taken into account, on comparing the constants a_0 of the gratings in both series of preparations.

§ 3. The probable constitution of the *silver-ultramarine* used being thus fixed now, this compound was prepared in greater quantities and its behaviour towards reactants which can substitute the Ag-atoms in it, was now studied in detail. In our previous paper we have already drawn attention to the fact that the substitution of the Na-atoms in *ultramarine* by Ag is probably a reaction tending to equilibrium, the final state depending on the concentration of the Ag-solution used. Even in the especially favourable case of the preparation of *Ag-ultramarine* from GUIMET's *blue* by means of $AgNO_3$ in solution, the final product appeared to contain always some *sodium*, — be it in very small quantities. No indication whatsoever was found of a charaçter of a certain inferior part of the six Na-atoms in the molecule deviating fundamentally from the others, as some investigators have eventually suggested.

According to HEUMANN [1]), the dissimilarity and lack of equivalence of the six Ag-atoms in *silver-ultramarine* would be demonstrated e.g. by the fact, that *not all the silver present* would be substituted by the corresponding amount of alcali-atoms, if boiled during a long time with solutions of the *alcali-chlorides* in excess. The substitution would proceed only until *two*

[1]) K. HEUMANN, Lieb. Ann. der Chemie, **201**, 265, 266, (1880); P. G. SILBER, Ber. d. d. chem. Ges., **14**, 941, (1881).

thirds of the total number of *Ag*-atoms present should be replaced by alcali-atoms. Our investigations have *not* corroborated this conclusion: on the contrary, in this case also there are only to be considered slowly proceeding reactions, tending to states of equilibrium between the solutions used and the solid *silver-ultramarine* in contact with them, without the occurrence of substitutions in simple stoechiometrical proportions of the *silver*-atoms by others, otherwise than quite accidentally.

In our experiments we started with the carefully purified and analysed *silver-ultramarine* prepared from GUIMET's *blue* N°. 7553, in the way formerly described, whose composition could best be described by means of the formula: $Ag_6 Al_6 Si_6 O_{30} S_3$. Its *Ag*-content was 43.9 % and, after repeated decantation, even somewhat lower (see above).

Of this preparation every times an equal quantity (7 grammes) was boiled in ERLENMEIJER-flasks with reflux-coolers during 50 hours with solutions of 20 times the theoretically necessary quantities of *LiCl*, *NaCl*, *KCl*, *RbBr* and *CsCl*. Soon it became evident, that the reaction in each case proceeded with highly deviating velocities: it occurred most rapidly in the case of the *Li*-, most slowly in the case of the *Cs*-salt, and with all salts regularly the more slowly, as the atomic weight of the alcali-metal increases. In the case of the *Li*-salt, already after 4 hours an intensively dark blue coloured substance was obtained, still containing 28.2 % *Ag*, — about half of the *Ag* present being replaced by *Li* therefore ($Ag_3 Li_3 Al_6 Si_6 O_{30} S_3$ requires: 25.82 % *Ag*); in a second experiment, which was continued during 50 hours, a dark dull violet preparation N°. 10 was obtained, which only contained 19.98 % *Ag* ($Ag_2 Si_4 Al_6 Si_6 O_{30} S_3$ requires: 18.72 % *Ag*). The colour of the other *ultramarines* obtained in this way on heating during 50 hours, was: in the case of *Na-Ag-ultramarine* (N°. 9) a dull greyish-blue (7.75 % *Ag*); in that of *K-Ag-ultramarine* (N°. 11), a somewhat clearer greyish-blue (20.5 % Ag); in the case of *Rb-Ag-ultramarine* (N°. 12) a slightly more greenish blue (22.2 % *Ag*); in that of *Cs-Ag-ultramarine* (N°. 13) a dull greyish yellow (38.9 % *Ag*).

The solutions of the *alcali-halogenides* used did not contain, even after 50 hours heating, any appreciable quantities of SiO_2 or Al_2O_3. The results of the analysis point to a composition of each of these products, as formed in the same time and under the same circumstances, which may be expressed by the following formulae:

in the case of N°. 10: a mixture of 82.3 % $Ag_2Li_4Al_6Si_6O_{30}S_3$ + 17.7 % $Ag_3Li_3Al_6Si_6O_{30}S_3$
in the case of N°. 9: a mixture of 18.7 % $Na_6Al_6Si_6O_{30}S_3$ + 81.3 % $AgNa_5Al_6Si_6O_{30}S_3$
in the case of N°. 11: a mixture of 48.7 % $Ag_2K_4Al_6Si_6O_{30}S_3$ + 51.3 % $Ag_3K_3Al_6Si_6O_{30}S_3$
in the case of N°. 12: a mixture of 93.2 % $Ag_3Rb_3Al_6Si_6O_{30}S_3$ + 6.8 % $Ag_4Rb_2Al_6Si_6O_{30}S_3$
in the case of N°. 13: a mixture of 36.1 % $Ag_5CsAl_6Si_6O_{30}S_3$ + 63.9 % $Ag_6Al_6Si_6O_{30}S_3$

The substitution of the *Ag*-atoms by the alcali-metal, therefore, does not only occur in the different cases considered with a highly different velocity, but it proceeds also in all cases until different limits are attained: with the *Na*-salt it is most complete, probably because these is only a slight

difference in the volume of the *Na*- and *Ag*-atoms and the mutual substitution is, therefore, effectuated in the easiest way. Subsequently the *Li-atom*, which gives 82.3 %, and the *K*-atom which gives 48.7 % of a *tetra-alcali*-substitution-product, come nearest to it; in the case of the *Rb*-salt the product obtained consists for 93.2 % of a *tri-alcali*-substitution-derivative, while in the case of the *Cs*-salt, almost $^2/_3$ of the *silver-ultramarine* appears *not* to be attached, — as is already indicated by its colour, — the other $^1/_3$ part being only transformed into a *mono*-substitution-product. In *no case, however, there appears to be present a certain limit for the substitution*, as HEUMANN suggested, who thought such a limit was reached as soon as $^2/_3$ of the *Ag*-atoms present were substituted by alcali-atoms.

§ 4. With the purpose to obtain further evidence of this, two series of experiments were started, in which every time equal weights (7 grammes) of the original *silver-ultramarine* were heated during 50 hours at 130° C. in sealed tubes, with in each case the 5 fold quantity of the salts *LiCl*, *NaCl*, *RbCl*, *KCl*, *$(NH_4)Cl$* and *CsJ*, and always *the same* quantity of *water* (10 grammes). In the second of experiments we used the salts: *LiI*, *NaI*, *KI*, *RbI*, *$(NH_4)I$* and *CsCl* in equivalent quantities and in the same molar concentrations, the heating being effectuated at 160° C. and during 50 hours. In the last series, moreover, one experiment was made also with *NaI*, not 5-times, but 10-times the theoretical quantity of it in the same weight of *water* being now used, with the special purpose of studying the influence of the concentration of *NaI* in this case. The products obtained were filtered off from the solutions, by means of *iodine-potassium-iodine-solutions* and a 10 % solution of *potassiumayanide* freed from *AgI* or *AgCl*, extracted with *carbondisulphide* with the purpose to eliminate traces of free *sulphur* eventually present, and were finally repeatedly washed with water and decanted. In the purest fraction thus obtained, the *Ag*-content was now determined by analysis. Also in these cases no appreciable formation of *SiO_2* and *Al_2O_3* appeared to have taken place, notwithstanding the prolongated heating: only in the tubes heated at 160° C. a slight excess of free sulphur could be stated. The results obtained are put together in the following table: See pag. 891.

The product N°. 9e, obtained from 7 Gr. of *silver-ultramarine* + 45 Gr. *NaI* + 10 Gr. *water* at 160° C. and 50 hours heating, did not differ appreciably in its colour from that of the preparation 9a. The colour was slightly clearer; its *Ag-content* appeared, on analysis, to be: 1.1 % *Ag* only. It may be considered as a mixture [1]) of 88.5 % *$Na_6 Al_6 Si_6 O_{30} S_3$* + 11.5 % *$Na_5 Ag Al_6 Si_6 O_{30} S_3$*. It becomes evident, therefore, that the yield of the compound: *$Na_6 Al_6 Si_6 O_{30} S_3$* is increased from 67.5 % to

[1]) According to this composition the preparation must contain 9.11 % *S*; a direct analysis gave: 9.24 % *S*.

CHLORIDES:

N°. 10*a*. **LiCl.** 7 Gr. *Ag-ultramarine* + 6.4 Gr. *LiCl* + 10 Gr. *water*, 50 hours at 130° C. Colour of the purified product: *dark violet-grey*; *Ag*-content: 15.6 %. A mixture of:

36.9 % $Li_5AgAl_6Si_6O_{30}S_3$ + 63.1 % $Li_4Ag_2Al_6Si_6O_{30}S_3$,

$a_0 = 8.71$ *A.U.*

N°. 9*a*. **NaCl.** 7 Gr. *Ag-ultramarine* + 8.7 Gr. *NaCl* + 10 Gr. *water*; 50 hours at 130° C. Colour of the purified product: *dull marine-blue*; *Ag*-content: 16.5 %. A mixture of:

15 % $Na_5AgAl_6Si_6O_{30}S_3$ + 85 % $Li_4Ag_2Al_6Si_6O_{30}S_3$.

$a_0 = 9.02$ *A.U.*

N°. 11*a*. **KCl.** 7 Gr. *Ag-ultramarine* + 11.2 Gr. *KCl* + 10 Gr. *water*; 50 hours at 130° C. Colour of the product obtained: somewhat *darker blue* than the *Na*-compound; *Ag*-content: 18.6 %. A mixture of:

24.6 % $K_4Ag_2Al_6Si_6O_{30}S_3$ + 75.4 % $K_3Ag_3Al_6Si_6O_{30}S_3$.

$a_0 = 9.13$ *A.U.*

N°. 80*a*. **(NH_4)Cl.** 7 Gr. *Ag-ultramarine* + 8.0 Gr. $(NH_4)Cl$ + 10 Gr. *water*; 50 hours at 130° C. Colour of the purified product: *olive green*. *Ag*-content: 22.7 %. A mixture [1]) of:

34.6 % $(NH_4)_4\,Ag_2\,Al_6\,Si_6\,O_{30}\,S_3$ +
+ 65.4 % $(NH_4)_3\,Ag_3\,Al_6\,Si_6\,O_{30}\,S_3$.

$a_0 = 9.18$ *A.U.*

N°. 12*a*. **RbCl.** 7 Gr. *Ag-ultramarine* + 18.1 Gr. *RbCl* + 10 Gr. *water*; 50 hours at 130° C. Colour of the purified product: *dull blue*; *Ag*-content: 24.4 %. A mixture of:

39 % $Rb_3Ag_3Al_6Si_6O_{30}S_3$ + 61 % $Rb_2Ag_4Al_6Si_6O_{30}S_3$.

$a_0 = 9.12$ *A.U.*

N°. 13*d*. **CsCl.** 7 Gr. *Ag-ultramarine* + 25.3 Gr. *CsCl* + 10 Gr. *water*; 50 hours at 160° C. Colour of the product obtained: *chrome-green*; *Ag*-content: 8.54 %. A mixture of:

67.9 % $Cs_5\,AgAl_6\,Si_6\,O_{30}\,S_3$ +
+ 32.1 % $Cs_4\,Ag_2\,Al_6\,Si_6\,O_{30}\,S_3$.

IODIDES:

N°. 10*d*. **LiJ.** 7 Gr. *Ag-ultramarine* + 20 Gr. *LiJ* + 10 Gr. *water*; 50 hours at 160° C. Colour of the product obtained: *dark violet*; *Ag*-content: 2.8 %. A mixture of:

72.2 % $Li_6Al_6Si_6O_{30}S_3$ + 27.8 % $Li_5AgAl_6Si_6O_{30}S_3$.

$a_0 = 8.67$ *A.U.*

N°. 9*d*. **NaJ.** 7 Gr. *Ag-ultramarine* + 24.5 Gr. *NaJ* + 10 Gr. *water*; 50 hours at 160° C. Colour of the product obtained: *vivid deep blue*; *Ag*-content: 3.1 %. A mixture of:

67.5 % $Na_6Al_6Si_6O_{30}S_3$ + 32.5 % $Na_5AgAl_6Si_6O_{30}S_3$.

$a_0 = 9.1$ *A.U.*

N°. 11*d*. **KJ.** 7 Gr. *Ag-ultramarine* + 22.9 Gr. *KJ* + 10 Gr. *water*; 50 hours at 160° G. Colour of the purified product: a *dull dark blue* (*marine-blue*); *Ag*-content: 4.3 %. Is a mixture of:

48.3 % $K_6Al_6Si_6O_{30}S_3$ + 51.7 % $K_5AgAl_6Si_6O_{30}S_3$.

N°. 80*d*. **(NH_4)J.** 7 Gr. *Ag-ultramarine* + 22 Gr. $(NH_4)J$ + 10 Gr. *water*; 50 hours at 160° C. Colour of the product obtained: *dark greenish-brown*; *Ag*-content: 12.3 %. On boiling with *NaOH ammonia* is set free, but only about 1/6 of the total quantity. A mixture of;

78.4 % $(NH_4)_5AgAl_6Si_6O_{30}S_3$ +
+ 21.6 % $(NH_4)_4Ag_2Al_6Si_6O_{80}S_3$.

$a_0 = 9.34$ *A.U.*

N°. 12*d*. **RbJ.** 7 Gr. *Ag-ultramarine* + 31.8 Gr. *RbJ* + 10 Gr. *water*; 50 hours at 160° C. Colour of the purified product: *dull very dark* till *black-blue*; *Ag*-content: 81.1 %; *S*-content: 7.08 %; calculated: 6.7 % *S*. A mixture of:

92.9 % $Rb_5AgAl_6Si_6O_{30}S_3$ + 7.1 % $Rb_4Ag_2Al_6S_6O_{30}S_3$.

$a_0 = 9.28$ *A.U.*

N°. 13*a*. **CsJ.** 7 Gr. *Ag-ultramarine* + 40 Gr. *CsJ* + 10 Gr. *water*; 50 hours at 130° C. Colour of the purified product; *dull greyish-blue*. *Ag*-content: 11.2 %. A mixture of:

27.6 % $Cs_5AgAl_6Si_6O_{30}S_3$ +
+ 72.4 % $Cs_4Ag_2Al_6Si_6O_{30}S_3$

$a_0 = 9.11$ *A.U.*

[1]) This preparation contained: about 4.2 % NH_3; calculated: 4.7 % NH_3.

88.5 % by the use of *twice* the concentration of *NaI* under the same conditions and with the same time of heating.

§ 5. From these experiments it becomes clear :

1°. That in using equal molar concentrations of the salt-solutions and, for the rest under equal circumstances, the substitution of *Ag* by the alcali-metals occurs in almost all cases *appreciably farther* in using the *iodides*, than in using the *chlorides*. (The only exception occurs with *caesium*) ; but this may be caused by the temperature of heating. We are controlling this fact once more).

2°. That the substitution of *Ag* by the alcali-metals (in casu : by *Na*) occurs under the same conditions of the experiment, *more completely, if the concentration of the salt-solution is kept higher.*

3°. That the substitution of the *Ag* present, under equal conditions of temperature, concentration and time of heating, occurs faster and completest, in the case of *Li*, and subsequently in that of *Na*, *K*, *Rb* and *Cs* in decreasing ratio, while the substitution by the radicle (NH_4) goes farther than in the case of the *K*-salt with $(NH_4)Cl$, but less far than with *KI*, if $(NH_4)I$ be used.

These results give a full proof of the fact that no upper limit exists for the substitution of Ag-atoms by alcali-atoms under these circumstances. There is merely question here of *equilibria*, of final states which are principally determined by the *concentrations* of the salt-solutions reacting with the *silver-ultramarine*. Moreover, these final states depend also on the special nature of the anions, which are linked to the alcali-atoms. The fact that the substitution in general goes farther in using the *iodides*, than in using the *chlorides*, is very probably connected with the much smaller solubility of *silver-iodide* in comparison with that of *silver-chloride*, — the active mass of the former in the solution thus being much smaller than that of the second compound. Under favourable circumstances practically *all Ag* of the *silver-ultramarine* may be substituted in this way by alcali-atoms. This behaviour is perfectly analogous to that observed in the case of the *permutites*, if salt-solutions react upon them.

§ 6. We have prepared a series of powder-spectrograms of all these preparations, using the improved cylindrical camera mentioned before, with a radius of 44.4 mm, and the α- and β-radiation of the *K*-series of a *copper-anticathode* under a voltage of 55000 Volts. The time of exposure was 2 or 3 hours. The results are indicated below : with the purpose to avoid tables as much as possible, we have communicated here only the observed diffraction-images with their indices and their relative, estimated intensities, which are printed behind the indices-symbol in fat figures ; also the grating-constants a_0 and the constants *A* and *B* of the quadratic equations for $sin^2 \frac{\theta}{2}$ in the case of the α- and β-radiations are mentioned at the

same time. The grating-constant a_0 appears, notwithstanding the differences in the intensities of the diffractions-images, to differ only slightly from the value of a_0 of GUIMET's *blue* itself. A number of graphs, in which the values of $(h^2 + k^2 + l^2)$ are taken as abscissae, while the relative estimated intensities of each diffraction-line are taken as ordinates, will enable an easier comparison of the spectrograms obtained with the different preparations studied in this way.

1. *Lithium-silver-Ultramarine* N°. 10.

(Contains: 19.98 % *Ag*).

Observed: {211} (8); {220} (1); {310} (α—8; β—1); {222} (4); {321} (6); {330}, {411} (5); {420} (2); {431}, {510} (2); {433}, {530} (α—3; β—1); {532}, {611} (α—3; β—1); {622} (2); {640} (2); {633}, {721} (1); {664} (2); {763} (2).

$A = 0{,}00767$; $B = 0{,}00623$. $a_0 = 8{,}79$ *A.U.*

2. *Lithium-silver-Ultramarine* N°. 15.

(Contains: 32.2 % *Ag*; was obtained from a *Li-Ag-ultramarine* by prolonged heating with an ammoniacal solution of *AgCl*).

Observed: {211} (8); {310} (α—7; β—1); {222} (5); {321} (6); {330} {411} (6); {431}, {510} (1); {440} (2); {433}, {530} (2); {600} (1); {532}, {611} (3); {633}, {721} (2); {730} (1).

$A = 0.00736$; $B = 0.00598$. $a_0 = 8.97$ *A.U.*

3.*i* *Potassium-silver-Ultramarine* N°. 11.

(Contains: 20.5 % *Ag*).

Observed: {211} (8); {220} (3); {310} (8); {222} (6); {321} (1); {330}, {411} (7); {413}, {510} (4); {440} (2); {433}, {530} (2); {600} (2); {532}, {611} (2); {622} (4); {444} (3); {543}, {505}, {710} (2); {633}, {721} (4).

$A = 0.00702$; $\beta = 0{,}00570$. $a_0 = 9{,}19$ *A.U.*

4. *Rubidium-silver-Ultramarine* N°. 12.

(Contains: 22.18 % *Ag*).

Observed: {211} (4); {310} (α—9; β—2); {222} (4); {321} (2); {330}, {411} (6); {440} (1); {433}, {530} (1); {600} (1); {532}, {611} (1); {622} (2); {444} (1); {633}, {721} (2).

$A = 0.00712$; $B = 0.00579$. $a_0 = 9.13$ *A.U.*

5. *Cesium-silver-Ultramarine* N°. 13.

(Contains: 38.92 % *Ag*).

Observed: {211} (2); {310} (α—8; β—2); {222} (4); {321} (4); {330}, {411} (6); {440} (2); {433}, {530} (2); {600} (2); {532}, {611} (2); {620} (2); {622} (2); {633}, {721} (4); {730} (1); {763} (2); {853} (1).

$A = 0.00731$; $B = 0.00594$. $a_0 = 9.01$ *A.U.*

In Fig. 1 the relative, estimated intensities of some of the most important diffraction-images are represented graphically. The upper graph relates to pure *Ag-ultramarine* (N°. 3); a comparison of the intensities, only

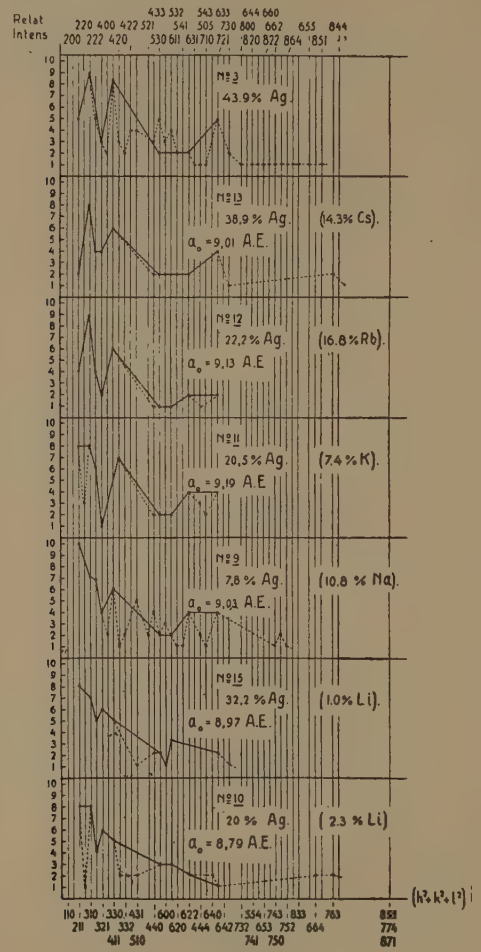

Fig. 1.

roughly estimated, may give some impression of the influence of an increasing *alcali*-content on the shape of the zigzag-line in its entire extension.

6. *Lithium-silver-Ultramarine N°.* 10^a.

(Contains: 15.6 % *Ag*; the diffraction-lines of this spectrogram are rather broad).

Observed: {211} (α—**10**; β—**2**); {310} (α—**6**; β—**2**); {222} (**4**); {321} (**5**); {330}, {411} (**4**); {332} (**1**); {431}, {510} (**3**); {440} (**4**); {600} (**2**); {532}, {611} (**2**); {541} (**1**); {622} (**2**); {543}, {505}, {710} (**3**); {655} (**1**).

$A = 0.00781$; $B = 0.00635$. $a_0 = 8.71$ *A.U.*

7. *Sodium-silver-Ultramarine* N^0. 9^a.

(Contains: 16.5 % *Ag*).

Observed: {211} (**9**); {310} (α—**6**; β—**1**); {222} (**5**); {321} (**1**); {400} (**4**); {330}, {411} (**4**); {332} (**2**); {431}, {510} (**2**); {440} (**3**); {433}, {530} (**2**); {600} (**2**); {532}, {611} (**1**); {444} (α—**2**; β—**1**); {622} (**3**); {633}, {721} (**4**); {730} (**1**); {752} (**1**); {763} (**1**); {853} (**1**).

$A = 0.00729$; $B = 0.00593$. $a_0 = 9.02$ *A.U.*

8. *Potassium-silver-Ultramarine* N^0. 11^a.

(Contains: 18.6 % *Ag*). The image was faint, but the diffraction-lines were sufficiently sharp.

Observed: {211} (α—**6**; β—**2**); {310} (α—**6**; β—**1**); {222} (**3**); {330}, {411} (α—**3**; β—**2**); {420} (**1**); {431}, {510} (**2**); {440} (**1**); {433}, {530} (**1**); {600} (**1**); {532}, {611} (**1**); {620} (**1**); {622} (**1**); {631} (**1**); {444} (**1**); {633}, {721} (**2**); {642} (**2**).

$A = 0.00711$; $B = 0.00578$. $a_0 = 9.13$ *A.U.*

9. *Rubidium-silver-Ultramarine* N^0. 12^a.

(Contains: 24.4 % *Ag*).

Observed: {211} (**7**); {310} (α—**8**; β—**2**); {222} (**4**); {321} (**1**); {330}, {411} (α—**4**; β—**2**); {420} (**1**); {431}, {510} (**1**); {440} (**2**); {433}, {530} (**1**); {600} (**1**); {532}, {611} (**1**); {620} (**1**); {622} (**2**); {444} (**1**); {633}, {721} (**2**); {642} (**2**); {844} (**1**).

$A = 0.00712$; $B = 0.00578$. $a_0 = 9.12$ *A.U.*

10. *Cesium-silver-Ultramarine* N^0. 13^a.

(Contains: 11,2 % *Ag*). A faint image with broad, vague lines.

Observed: {211} (**5**); {310} (α—**6**; β—**1**); {222} (**1**); {321} (**5**); {400} (**4**); {422} (**3**); {431}, {510} (**4**); {521} (**1**); {600} (**1**); {532}, {611} (**1**); {541} (**1**); {631} (**1**); {444} (**1**); {642} (**1**).

$A = 0.00714$; $B = 0.00580$. $a_0 = 9.11$ *A.U.*

(In this spectrogram an intense line was found, whose $sin^2 \frac{\theta}{2}$ was 0.0509; evidently this image must be ascribed to an impurity present). A later spectrogram has, indeed, conformed this.

11. *Lithium-silver-Ultramarine* N^0. 10^d.

(Contains: 2,8 % *Ag*).

Observed: {200} (**3**); {21}, α and β, (**10**; **2**); {310}, α and β (**5**; **2**); {222} (**6**); {321} (**4**); {330}, {411} (**4**); {332} (**2**); {510}, {431} (**4**); {521} (**1**); {440} (**5**); {530}, {433} (**2**); {600} (**2**); {532}, {611} (**3**); {550} (**3**); {633}, {721} (**3**); {730} (**1**); {840} (**1**); {655} (**1**); {851} (**1**).

$A = 0.00789$; $B = 0.00641$. $a_0 = 8.67$ *A.U.*

12. *Rubidium-silver-Ultramarine* N^0. 12^d.
(Contains: 8.1 % *Ag*).

Observed:
{211} (**8**); {310} (**7**); {222} (**6**); {330}, {411} (α—**6**; β—**1**); {431}, {510} (**5**); {440} (**2**); {433}, {530} (**2**); {600} (**3**); {532}, {611} (**2**); {622} (**4**); {444} (**2**); {543}, {505}, {710} (**1**); {633}, {721} (**3**).
$A = 0.00689$; $B = 0.00560$. $a_0 = 9.28$ *A.U.*

13. *Sodium-silver-Ultramarine* N^0. 9^d.
(Contains: 3.1 % *Ag*).

Observed: {211} (**10**); {310} (**5**); {222} (**6**); {321} (**2**); {330}, {411} (α—**5**; β—**2**); {400} (**3**); {332} (**2**); {431}, {510} (**5**); {433}, {530} (α—**2**; β—**1**); {521} (**1**); {440} (**3**); {600} (**2**); {532}, {611} (**2**); {622} (**4**); {631} (**1**); {444} (**2**); {543}, {505}, {710} (**2**); {633}, {721} (**3**); {730} (**1**); {732} (**1**); {662} (**2**); {840} (**2**).
$A = 0.00727$; $B = 0.00591$. $a_0 = 9.03$ *A.U.*

14. *Ammonium-silver-Ultramarine* N^0. 80^a.
(Contains: 22.7 % *Ag*). A faint image with broad, vague lines.

Observed: {211} (**3**); {310} (α—**7**; β—**1**); {222} (**4**); {330}, {411} (α—**3**; β—**1**); {420} (**1**); {332} (**1**); {431}, {510} (**2**); {433}, {530} (**2**); {600} (**1**); {620} (**1**); {631} (**1**); {444} (**1**). The higher indices are uncertain.
$A = 0.00703$; $B = 0.00571$. $a_0 = 9.18$ *A.U.*

15. *Ammonium-silver-Ultramarine* N^0. 80^d.
(Contains: 12.3 % *Ag*). Faint, badly formed and unsharp image.

Observed: {211} (**8**); {310} (**1**); {222} (**2**); {321} (**2**); {400} (**1**); {420} (**3**); {422} (**3**). The higher indices are uncertain.
$A = 0.00680$; $B = 0.00553$. $a_0 = 9.34$ *A.U.*

Of both the last mentioned preparations we have also taken two spectrograms with a time of exposure of 4 hours. They were not much sharper than the ones described above, besides a series of uncertain indices, we found: $a_0 = 9.11$ A.U. for the first, and 9.23 A.U. for the last substance. In every case it seems, that the grating-constant increases, if more of the (NH_4)-radicle be substituted for *Ag*. Remarkable is not only the faintness of the images, but also the fact, that all images with the higher values of the square-indices-sums are lacking. It is not improbable that a partial dislocation of the periodical structure is caused by the reaction with these *ammonia*-salts.

§ 7. On comparing a_0 of the different *alcali-silver-ultramarines*, it may be remarked, that:

1⁰. The introduction of *Li* in the place of *Ag*, the grating-constant a_0 clearly decreases with increasing amount of *Li*: $a_0 = 8.96$ A.U. in *Ag-ultramarine* decreases by substitution of more *Li* gradually to: 8.79, then to 8.71 and finally to 8.67 A.U.

2⁰. The substitution of *Li* by *Na* or *K*, etc., effectuates an increase of a_0, which attains a maximum by substitution by *K* or *Rb* and decreases again a little, if *Rb* or *Cs* is introduced: with *Li*: $a_0 = 8.79$ A.U.; with *Na*: $a_0 = 9.02$—9.1 A.U.; with *K*: $a_0 = 9.13$—9.19 A.U.; with *Rb*: $a_0 = 9.12$—9.25 A.U.; with *Cs*: $a_0 = 9.11$ A.U. However, the differences are only very small.

3⁰. The substitution by (NH_4) causes an increase of the grating-

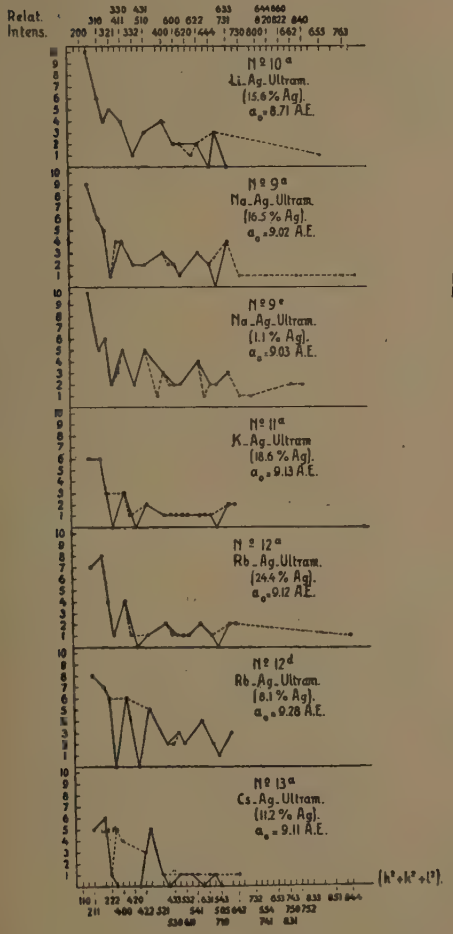

Fig. 2a

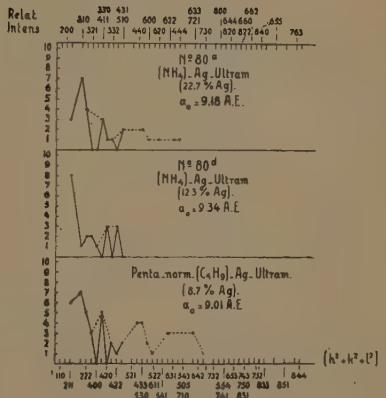

Fig. 2b

constant, which is intermediate between the influence exerted by *K* and *Rb* [1]) ; the influence of (NH_4) in this respect is certainly stronger than that of *Na*.

4°. In the same kind of *alcali*-substitutionproducts there are not always the same diffraction-images present, if the time of exposure is the same, but it is not possible to indicate a regular connection between the *alcali*-content and the increase of the intensity of the same interference-maxima.

5°. On comparing the different *alcali*-substitutionproducts, the relative intensities of the most important diffraction-images are certainly modified (see Fig. 2*a* and 2*b*), without it being possible, however, to deduce general relations between these variations.

§ 8. HEUMANN (loco at.) has also emphazised, that on melting *silver-ultramarine* in a crucible with an excess of the *alcali-halogenides*, — preferably with the *iodides*, — *all silver* may be substituted by the *alcali*-metals, thus beautiful *alcali-ultramarines* of varied composition being regenerated. We found, that also this conclusion must be considered as erroneous : at first view already the colour of the reaction-products obtained in this way and purified in the way already repeatedly mentioned, appeared to differ conspicuously from that of a pure *alcali-ultramarine* ; in the case of the *Na*-compound, for instance, this can be easily verified.

The experiments were made in this way, that small quantities of *silver-ultramarine* with a *silver*-content of 43.9 % were melted with 30- or 40-times the equivalent quantities of the pure, anhydrous *iodides* of *Li, Na, K, Rb, Cs*, etc. in covered, small porcelain crucibles, the reacting substances being first finely powdered and thoroughly intermixed. The crucibles were kept during a considerable time just a little above the melting points of the *iodides* used. After cooling, the blue mass obtained was solved in water, the residue filtered off and thoroughly washed, and then extracted several times with a 20 % solution of *potassiumcyanide* at 70° C., until no *AgJ* was any more present. Then the product was carefully washed and purified by repeated decantations ; finally it was dried at 100° C. Analysis of these products, after thoroughly drying at 130° C. taught us, that they contained almost in every case a certain quantity of *Ag*, as the somewhat duller colour, in comparison with that of the pure *alcali-ultramarines*, indicated already beforehand. In this way it could be proved for example, that preparation N°. 5 contained, besides *Li*, also 11.5 % *Ag* ; preparation N°. 4*, besides *Na*, also 8 % *Ag* ; preparation N°. 6, besides *K*, also 11.24 % *Ag* ; preparation N°. 7, besides *Rb*, also 2.7 % *Ag* ; and preparation N°. 8, besides *Cs*, still 4.3 % *Ag*. Increasing the time of melting, did not alter this phenomenon. The compositions mentioned above,

[1]) From TUTTON's wellknown investigations on the influence of the isomorphous substitution of the *alcali*-metals by the (NH_4)-radicle on the size of the crystalparameters, it has become evident, that there the influence of the (NH_4)-radicle is intermediate between that of *Rb* and *Cs*.

correspond : in preparation N°. 5 to a mixture of 85.3 % of a *penta-lithium-silver-ultramarine* + 14.7 % of a *tetra-lithium-diargento-ultramarine* ; in preparation N°. 4* : to a mixture of 16.1 % *Na-ultramarine* + 83.9 % of a *penta-sodiumsilver-ultramarine* ; in N°. 6 : to a mixture of 70.6 % *penta-potassium-silver-ultramarine* + 29.4 % *tetra-potassium-diargento-ultramarine* ; while the preparations N°. 7 and 8 for their greater part, i.e. for 63.9 %, respectively 67.0 %, appeared to consist of *Rb-*, respectively *Cs-ultramarines*, + 36.1 resp. 33 % *penta-alcali-silver-ultramarines*.

The spectrographical study of these derivatives by means of *X*-rays gave the following results :

16. *Lithium-silver-Ultramarine N°.* 5.
(Contains: 11,5 °/₀ *Ag*).

Observed: {200} (**6**); {211} (α—**10**; β—**3**); {310} (α—**5**; β—**2**); {222} (**7**); {321} (**4**); {330}, {411} (**3**); {332} (**2**); {422} (**2**); {510}, {431} (**5**); {521} (**1**); {440} (**5**); {530}, {433} (**2**); {600} (**2**); {532}, {611} (**2**); {541} (**1**); {622} (**4**); {631} (**1**); {633}, {721} (**3**); {730} (**1**).

$A = 0{,}00772$; $B = 0{,}00628$. $a_0 = 8{,}76$ *A.U.*

17. *Sodium-silver-Ultramarine N°.* 4*.
(Contains: 8 °/₀ *Ag*).

Observed: {211} (**10**); {310} (α—**7**; β—**1**); {222} (**7**); {321} (**4**); {330}, {411} (α—**5**; β—**1**); {431}, {510} (**5**); {433}, {530} (α—**3**; β—**1**); {521} (**1**); {440} (**4**); {600} (**3**); {532}, {611} (**3**); {622} (**4**); {631} (**1**); {444} (**2**); {543}, {505}, {710} (**1**); {633}, {721} (**3**); {662} (**2**).

$A = 0{,}00719$; $B = 0{,}00584$. $a_0 = 9{,}08$ *A.U.*

18. *Potassium-silver-Ultramarine N°.* 6.
(Contains: 11,24 °/₀ *Ag*).

Observed: {211} (α—**10**; β—**3**); {310} (α—**6**; β—**2**); {222} (**6**); {321} (**2**); {400} (**3**); {330}, {411} (**6**); {420} (**1**); {332} (**1**); {431}, {510} (**5**); {433}, {530} (α—**4**; β—**1**); {521} (**1**); {440} (**3**); {600} (**4**); {532}, {611} (**4**); {622} (**5**); {444} (**4**); {543}, {505}, {710} (**4**); {633}, {721} (**5**); {750}, {743}, {831} (**2**); {662} (**2**); {752} (**2**); {840} (**1**); {655} (**1**); {851} (**1**); {844} (**1**); {855} (**2**).

$A = 0{,}00694$; $B = 0{,}00564$. $a_0 = 9{,}24$ *A.U.*

19. *Rubidium-silver-Ultramarine N°.* 7.
(Contains: 2,7 °/₀ *Ag*).

Observed: {211} (**7**); {310} (α—**7**; β—**1**); {222} (**6**); {330}, {411} (α—**6**; β—**1**); {400} (**1**); {431}, {510} (**5**); {440} (**3**); {433}, {530} (**2**); {600} (**4**); {532}, {611} (**3**); {622} (**5**); {444} (**3**); {543}, {505}, {710} (**2**); {633}, {721} (**5**).

$A = 0{,}00699$; $B = 0{,}00568$. $a_0 = 9{,}21$ *A.U.*

20. *Cesium-silver-Ultramarine* N°. 8.
(Contains: 4,3 % *Ag*). A faint, very hazy and vague image.
Observed: {211} (5); {310} (*α*—5; *β*—1); {222} (2); {332} (4); {431}, {510} (2); {521} (1); {730} (2).
$A = 0{,}00710$; $B = 0{,}00577$. $a_0 = 9{,}14$ *A.U.*

From these data our former remarks about the influence of the subsequent substitutions: *Li*→*Na*→*K*→*Rb*→*Cs* on the value of the grating-constant a_0 appear to be corroborated here very distinctly: while a_0 for the *Li*-compound appears to be even smaller than for *Ag-ultramarine*, it becomes greater in the *Na*-compound, increases again in the *K*-substitution-product, till a maximum of 9.24 A.U. is reached, and then decreases in the *Rb-ultramarine* (9.21 A.U.), until in the *Cs*-derivative the value of the *Na-ultramarine* is reached once more. This happens, notwithstanding the *Ag*-content of the *Rb*- and *Cs*-compounds is appreciably *smaller* than for instance in the *K-Ag*-derivative. The influence of the substitution of the *alcali*-metals on the relative intensities of the corresponding diffraction-images is best seen from the graphs in Fig. 3 (only for the *α*-radiation). The great changes in intensity of the subsequent diffraction-lines in the spectrogram of the *Li*-derivative, — which in this respect strongly resembles the *Ag-ultramarine* itself, — are gradually diminished and effaced by subsequent substitution by *Na*, *K* and *Rb*, as may be seen, for instance, on comparing the intensities of (222). The image of the *Cs*-compound is, as has been already said, very faint and rudimentary.

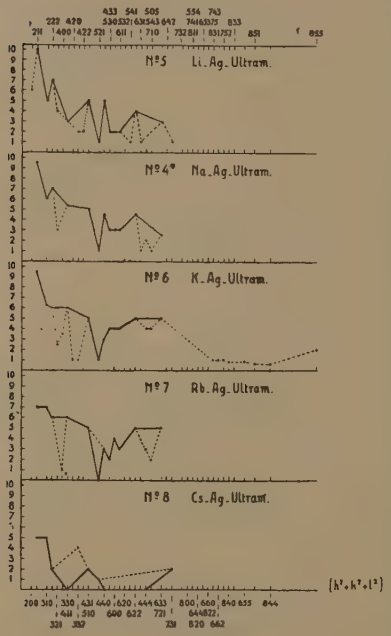

Fig. 3.

§ **9.** The highly remarkable fact must be emphasized here, *that the Ag-compounds of all other ultramarines, — e.g. of the green, red, pink and violet ones of French, as well as of German origin, always give, after melting them with, for example Na I, in excess, ultramarine-blues, independent of the original colour of the ultramarines from which the Ag-salts were prepared.* In *no* case an *ultramarine* of the same colour as the original one was obtained. Thus, e.g. from the *Ag*-salts of *pale rose* coloured *ultramarines* (with 13.3 %, 22.7 % and 34 % *Ag*), *cobaltblue*

or *pale blue Na-ultramarines* were generated; from the *Ag*-salts of *red* and *violet* ultramarines (*Ag*-content: 29 % and 35 %), *ultramarines* of a *vivid deep blue* colour were produced. The blue colour of the product obtained is the more lucid and lustrous, the higher the *Ag*-content was of the original *Ag-ultramarines*. From the *Ag*-salts of the *ultramarine-greens* (with 51 %, respectively 49.6 % *Ag*), dark *greenish blue* or *blue-green Na-ultramarines* were regenerated: of all kinds of *ultramarines* besides the true blue ones, the *green ultramarines* seem to be closest to autonomical chemical individuals and to be the best proof against the attack of concentrated solutions at 130° or 160° C. or of that of molten *iodides*.

§ **10.** From the preparation N°. 5, which corresponded, as was already remarked, to a mixture of 85.3 % $Li_5AgAl_6Si_6O_{30}S_3$ + 14.7 % $Li_4Ag_2Al_6Si_6O_{30}S_3$, we obtained by prolongated heating with an ammoniacal solution of *Ag Cl* a product N°. 15, whose *Ag*-content had now become 32.2 %. The composition of this product, the grating-constant a_0 of which was: 8.97 A.U. (see Fig. 1), corresponds to a mixture of 93.5 % $Li_2 Ag_4 Al_6 Si_6 O_{30} S_3$ and of 6.5 % $Li Ag_5 Al_6 Si_6 O_{30} S_3$.

§ **11.** Of course, the *alcali-silver-ultramarines* described in the above, may, in their turn, again be melted with an excess of other *alcali-iodides*; it is possible in this way to obtain a series of *mixed alcali-silver-ultramarines*, or eventually also *silverfree* mixed *alcali-ultramarines*.

Thus, by melting *Li-Ag-ultramarine* N°. 10 (19.98 % *Ag*) with an excess of *RbJ*, a blue *Li-Rb-Ag-ultramarine* N°. 36[z], with a *silver*content of 5 % was obtained; with respect to its origin, this may be considered to be a mixture of 53 % $Li_4 Rb AgAl_6Si_6O_{30}S_3$ + 29.3 % $Li_4Rb_2Al_6Si_6O_{30}S_3$ + 17.7 % $Li_3 Rb_3 Al_6 Si_6 O_{30} S_3$.

In the same way from *Rb-Ag-ultramarine* N°. 12 (with 22.2 % *Ag*), a *Rb-Li-Ag-ultramarine* (N°. 28[z]) was obtained by melting with *LiJ*; the beautifully blue coloured preparation appeared to have still an *Ag*-content of 4.2 %, and may be considered to consist of a mixture of 50 % $Rb_3Li_2AgAl_6Si_6O_{30}S_3$ + 43.2 % $Rb_3Li_3Al_6Si_6O_{30}S_3$ + 6.8 % $Li_4Rb_2Al_6Si_6O_{30}S_3$.

Also the *Li-Ag-ultramarine* N°. 15 of § 9 (with 32.2 % *Ag*) was, by melting with *RbJ*, transformed into a vividly blue coloured *Rb-Li-ultramarine* (N°. 61), which appeared to be completely *silverfree*, and to which, by its origin, a constitution must ascribed of a mixture of 6.5 % $Rb_5 Li Al_6 Si_6 O_{30} S_3$ + 93.5 % $Rb_4 Li_2 Al_6 Si_6 O_{30} S_3$.

From the preparation 19[1] mentioned in our previous paper (with 39.4 % *Ag*), by melting it with an excess of *RbJ*, a beautiful, blue coloured *Rb-Na-Ag-ultramarine* N°. 73 (with 8.9 % *Ag*) was obtained; perhaps its constitution might be considered to be: 4.4 % $Rb_5 Na Al_4 Si_6 O_{24} S_3$ + 60 % $Rb_4 Na Ag Al_4 Si_6 O_{24} S_3$ + 35.6 % $Rb_3 Na_2 Ag Al_4 Si_6 O_{24} S_3$; etc. Also in the cases considered, no appreciable formation of SiO_2 or Al_2O_3 during the reaction was observed.

Finally, from the compound 4*, which is a *Na-Ag-ultramarine* with 8 % *Ag*, a beautiful blue preparation N⁰. 35ᵃ was obtained by melting it with an excess of *RbJ*; this *Na-Rb-Ag-ultramarine*, which appeared still to contain 3.2 % *Ag*, may be considered as mixture of 16.1 % $Na_6 Al_6 Si_6 O_{30} S_3$+50.9% $Na_5RbAl_6Si_6O_{30}S_3$+33 % $Na_5AgAl_6Si_6O_{30}S_3$; etc.

The results of the ROENTGEN-spectroscopic investigation of all these products are communicated in the following tables:

21. *Lithium-rubidium-silver-Ultramarine* N⁰. 36ᵃ.

(Contains: 5.0 % *Ag*).

Observed: {211} (**8**); {310} (*α*—**7**; *β*—**4**); {222} (**6**); {321} (**2**); {330}, {411} (**4**); {431}, {510} (*α*—**3**; *β*—**1**); {620} (**1**).

$A = 0.00724$; $\beta = 0.00588$. $a_0 = 9.05$ *A.U.*

22. *Rubidium-lithium-silver-Ultramarine* N⁰. 28ᵃ.

(Contains: 4.2 % *Ag*).

Observed: {211} (*α*—**10**; *β*—**3**); {310} (*α*—**3**; *β*—**1**); {222} (**6**); {321} (**2**); {330}, {411} (**3**); {420} (**1**); {332} (**1**); {431}, {510} (**3**); {440} (**2**); {532}, {611} (**1**); {622} (**1**).

$A = 0.00789$; $B = 0.00641$. $a_0 = 8{,}67$ *A.U.*

23. *Rubidium-lithium-Ultramarine* N⁰. 61.

(Contains *no* more *Ag*).

Observed: {110} (**2**); {211} (*α*—**10**; *β*—**3**); {310} (*α*—**6**; *β*—**2**); {222} (**6**); {321} (**1**); {330}, {411} (*α*—**5**; *β*—**1**); {400} (**2**); {431}, {510} (**4**); {440} (**2**); {433}, {530} (**2**); {600} (**2**); {532}, {611} (**2**); {620} (**1**); {541} (**1**); {622} (**4**); {444} (**2**); {505}, {543}, {710} (**1**); {633}, {721} (**4**); {750}, {743}, {831} (**1**); {662} (**1**); {840} (**1**).

$A = 0.00720$; $B = 0.00585$. $a_0 = 9.07$ *A.U.*

24. *Rubidium-sodium-silver-Ultramarine* N⁰. 73.

(Contains: 8.9 % *Ag*).

Observed: {211} (*α*—**7**; *β*—**2**); {310} (*α*—**5**; *β*—**2**); {222} (**4**); {321} (**2**); {330}, {411} (**3**); {420} (**1**); {332} (**1**); {431}, {510} (**3**); {433}, {530} (**1**); {600} (**1**); {532}, {611} (**1**); {620} (**1**); {631} (**2**); {642} (**1**).

$A = 0.00705$; $\beta = 0.00573$. $a_0 = 9.17$ *A.U.*

25. *Sodium-rubidium-silver-Ultramarine* N⁰ 35ᵃ.

(Contains: 3.2 % *Ag*).

Observed: {211} (*α*—**9**; *β*—**2**); {310} (*α*—**5**; *β*—**2**); {222} (**6**); {321} (**1**); {400} (**2**); {330}, {411} (**3**); {413}, {510} (*α*—**3**; *β*—**1**); {521} (**1**); {440} (**2**); {433}, {530} (**2**); {600} (**2**); {532}, {611} (**2**); {622} (**3**); {444} (**1**); {505}, {543}, {710} (**1**); {633}, {721} (**2**).

$A = 0.00728$; $B = 0.00591$. $a_0 = 9.02$ *A.U.*

As is seen from Fig. 4, there cannot be stated a pronounced regularity in the typical decrease of the intensities of the subsequent, corresponding diffraction-images of these *X*-ray-patterns.

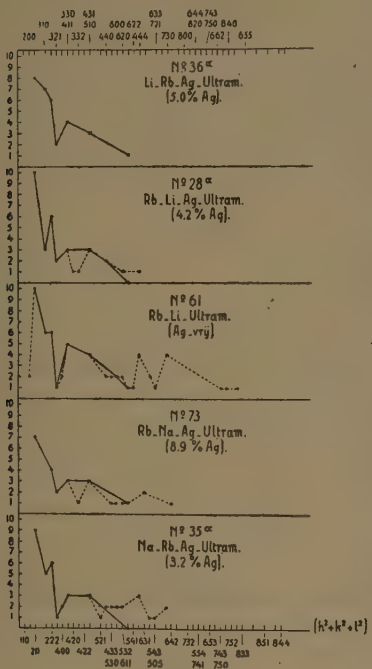

Fig. 4.

§ **12.** It is also possible to obtain derivatives of the *bivalent* metals *Mg, Ca, Sr, Ba, Zn, Mn,* etc., by melting the *Ag-ultramarine* with an excess of the *iodides* of these metals. About the thus obtained preparations and their *X*-ray-spectrograms we will publish the relative data later-on in a separate paper. We wish here only to remark, that the blue colour of the alcali-ultramarines has disappeared completely in these products: they are olive- or dull green, pale and dark grey, and even white.

However, in every case it has by these investigations now become quite evident, that *all* reactions connected with the substitution of the *Ag*-atoms in the *Ag-ultramarine* prepared from GUIMET's *blue* Nº. 7553, are really reactions tending to certain states of *equilibrium*; the finally reached degree of substitution depends in all cases investigated on the special nature and the concentrations of the salt-solutions brought into contact with the *Ag-ultramarine*, and also on the temperature and the duration of the reaction.

§ **13.** This last fact manifests itself also very clearly in the case, in which *organic iodides: methyl-, ethyl-, butyl-iodides,* etc. are made to react with the *Ag-ultramarine*. Thus, for instance, we made *three* times the necessary, calculated quantity of *normal butyl-iodide* react during 50 hours at 130° C. with a carefully dried preparation of *Ag-ultramarine*. The reaction-product was first purified by extraction with *benzene*, to eliminate the excess of *butyl-iodide*, and then the residue was freed from *Ag]* in the usual way. The product obtained was a *dull green ultramarine* (with 38.6 % *Ag*); if treated in the same way with the same relative quantity of *normal butyl-iodide* once more at 130° C. during 50 hours, there resulted a product of a *greenish grey* colour, which appeared, after purification, to contain now only 29.6 % *Ag*. While the product obtained in the first reaction corresponds to about: 47.8 % unaltered *Ag-ultramarine* + 52.2 % $(C_4H_9)Ag_5Al_6Si_6O_{30}S_3$, — that obtained in the last reaction corresponds exactly to: $(C_4H_9)_2Ag_4Al_6Si_6O_{30}S_3$, which requires: 29.68 % *Ag*.

This last compound was now heated once more in the same way, but this time with *five* times the quantity of *butyl-iodide* necessary for a complete substitution of all *Ag*-atoms, during 50 hours at 160° C. The resulting, *violet-grey* product appeared now to contain only 8.7 % *Ag* and its composition, therefore, corresponds to a mixture of about 97.1 % $(C_4H_9)_5AgAl_6Si_6O_{30}S_3$ + 2.9 % $(C_4H_9)_4Ag_2Al_6Si_6O_{30}S_3$. The original *silver-ultramarine* is, therefore, practically transformed into a *penta-norm.-butyl-silver-ultramarine*. Of this preparation a powder-spectrogram was made in the same way as in the case of the other compounds. The results were as follows :

26. *Penta- norm. Butyl-Silver-Ultramarine.*

(Contains: 8.7 % *Ag*; on heating, the odour of *butyl-sulphide* is strongly noticeable).

Observed: {211}(**6**); {310}(**7**); {222}(**5**); {321}(**3**); {330}, {411} (α—**5**; β—**2**); {332}(**2**); {422}(**1**); {431}, {510}(**2**); {440}(**4**); {433}, {530}(**4**); {600}(**2**); {532}, {611} (**1**); {622}(**3**); {633}, {721}(**3**); {730}(**1**).

$$A = 0.00731\,;\ B = 0.00594. \qquad a_0 = 9.01\ A.U.$$

The spectrogram obtained is completely analogous to that of the other *ultramarines* (see Fig. 2*b*) : it becomes clear, that even the introduction of *five butyl*-radicles into the molecule, does *not* change the general structure of these remarkable substances ; a clear relation between the constitution of all these compounds and the change in the intensities of the corresponding diffraction-images, however, cannot be stated as yet.

In all the investigations published here, it has, alas, become evident, that even with the most variegated substitutions, the changes of the structure of all these *ultramarine*-derivatives are relatively too small ; and that the changes of intensity of corresponding diffraction-lines in the spectrograms are so whimsical, that it seems almost hopeless to draw farther conclusions from these facts about the precise architecture of these interesting substances.

The study of the organic substitution-products is now continued by us.

Groningen, Laboratory for Inorganic and Physical Chemistry of the State-University.

Chemistry. — *On the Exact Determination of the Specific Heat of Solid Substances between 0° and 1625° C. I. Method and Apparatus.* By Prof. Dr. F. M. JAEGER and Dr. E. ROSENBOHM.

(Communicated at the meeting of September 24, 1927).

§ 1. In connection with the development of the modern theories concerning the specific heat of solid substances, during the last decennia the attention of numerous investigators has again been drawn more particularly to this physical quantity, which, since the classic investigations of DULONG and PETIT and the establishment of the empirical rule named after them, has become of so much interest also to chemists.

In connection with a series of investigations made in this laboratory with the purpose of developing a number of methods of measurement of several physical constants, allowing the exact and reproducible determination of these constants also at high temperatures, — we have during the last years developed i.a. a method for the accurate measurement of the specific heats of solid substances under constant pressure. This method, which has been tested now by us in the case of several substances, has appeared to enable us to determine the specific heats mentioned with a degree of accuracy, which under favourable circumstances, even at very high temperatures may attain about 0.001 of the determined value.

We intend to test experimentally the validity of the modern theories in this way up to these high temperatures in a number of cases, and especially to study the variation of the so-called "atomic heat" of the solid elements with the temperature, also under these extreme conditions. In the following we give the description of the apparatus used and of the method of experimenting followed by us.

§ 2. The principle of the metal-calorimeter was made use of here, after the manner originally proposed by NERNST, KOREF and LINDEMANN [1]) and as applied more in particular also to measurements at temperatures up to 900° C. by MAGNUS [2]). During the construction of the apparatus, the experiences of many investigators, more in particular of WHITE, were borne in mind. Besides, all improvements necessary for our purpose were made, so that the instrument and the method followed have now reached a very high degree of perfection.

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[1]) Compare: Sitz. Ber. d. preus. Akad. d. Wiss. Berlin, (1910), 247; Ann. der Physik, **36**, 49, (1911).

[2]) A. MAGNUS, Phys. Zeits., **14**, 5, (1913); Ann. der Physik, (4) **70**, 303, (1923); A. MAGNUS and A. HODLER, Ann. der Physik, (4), **80**, 808, (1926).

In Fig. 1 the arrangement of the calorimeter used by us has been represented diagrammatically [1]). A double-walled prismatic vessel O, made

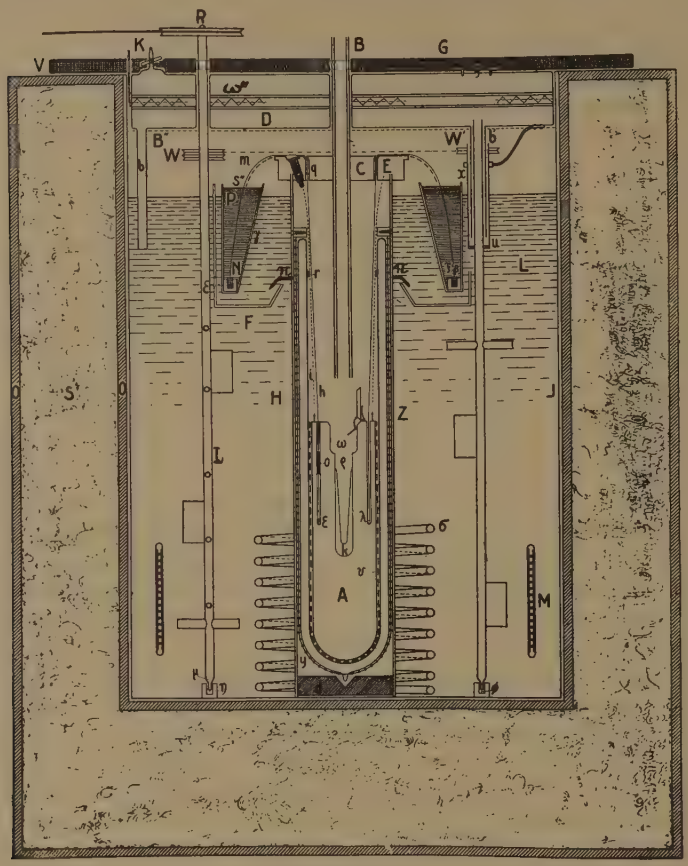

Fig. 1.

of thick wood, the outside measurements of which are $95 \times 95 \times 100$ cm., the inside measurements $65 \times 65 \times 81$ cm., whose interspace is completely filled out with slag wool S, forms, together wich a water-reservoir of great capacity placed in it, the insulation of the calorimeter from the surrounding. The water-reservoir is provided with a water-bearing cover and covered with a layer V of felt several cms. thick. The surrounding space is, moreover, maintained as much as possible at a constant temperature. In this vessel a zinc vessel J has been placed which impinges on its walls and

[1]) In the construction of the calorimeter we were assisted in an excellent manner by the nstrumentmaker of the laboratory, Mr. A. VAN DER MEULEN.

measures 65 × 65 × 81 cms. It contains the water surrounding the calorimeter, about 260 Liters, the surface of which rises to about 62 cm. from the bottom. This water-reservoir can be shut by a water-bearing cover *D*, which is supported by iron hoops *B''*. The cover is about 7 cms. high and contains about 29 Liters water, which is forced up from the calorimeter-vessel *J* (see below) and flows back in it by constant circulation. The water is maintained at a constant temperature by means of three heating-spirals *M* of nickelwire, which have been spread out in flat tight soldered brass boxes 0.5 cm. thick ; also with the aid of a spiral tube σ, with circulating cooling water, and of a large thermoregulator *Th*. The arrangement to bring the circulating water into motion, consists of three centrifugal stirrers *l*. These stirrers consist of brass tubes 1.2 cms. wide, are provided with small holes, and are at different heights, supplied with *T*-pieces, the arms of which are about 20 cms. long and out of which the water is hurled with force through the rotation of the stirrers. About 5 cms. above the level of the water the tubes are provided with wooden disks *W* and *W'*, which are interconnected by driving-belts. These driving-belts have been made of spiral-strings of brass-wire and are rotated by being connected with an other disk *R*, which is set in motion by an electromotor. The axes of rotation of the stirrers are provided at the bottom with steel points μ, which rotate in bearings of agate φ; these bearings are fixed in brass cushions η, which are firmly soldered to the bottom of the vessel *J*. Also after a very long use the stirrers thus fitted proved to work perfectly and without any disturbance ; the water does not in any way interfere with the rotation of the shaft-ends in their bearings. The third stirrer *W'* has a construction somewhat different from the other two (for further particulars see below).

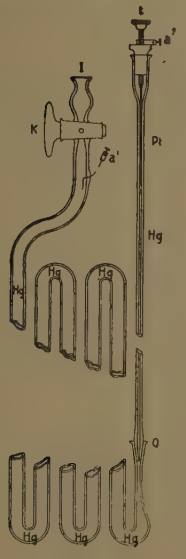

Fig. 2.

For the heating of the water in the reservoir served the above-mentioned heating-spirals *M*, two of which are interconnected. With the help of adjustable resistances, they keep the water just a little below 20° C. The third heating-spiral, however, is connected with a large thermo-regulator *Th.*, which, as is shown in Fig. 2, consists of a glass tube bent four times alternately upward and downward and terminating in a tube narrowed to a capillary ; the regulator is entirely filled with six kilogrammes of purest mercury. To this regulator a number of relays are connected according to the wiring-diagram given in Fig. 3 [1]). It is essential to prevent in the electric thermo-regulator as much as possible the flashing of an induction-spark at the

[1]) Let A_1, A_2 and A_3 represent three accumulators: W_1 to W_8 are adjustable and constant lamp-resistances; R_1, R_2, R_3 are three relays. The current-circuit of A_2 is always closed on relays R_1, with little strength of current only. If e.g. R_1 turns to the right, the

breaking of the contact between platinum-pin and thread of mercury. This was achieved by the system of relays as is shown diagrammatically in

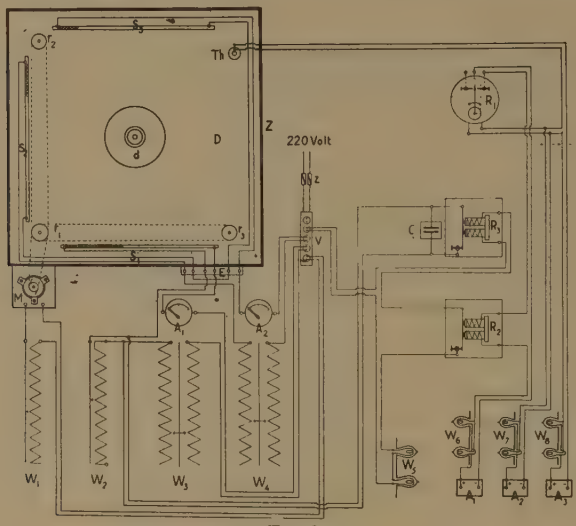

Fig. 3.

Fig. 3 ; by this arrangement the working of the regulator was regulated only by a very small fraction of the heating-current (2 Volt ; 2 milli-Ampère) and each oscillation of temperature above or below 20° C. was compensated almost immediately. The cooling-spiral σ likewise helped to bring about this result. An adjustable current of cold water flows through it very slowly ; the spiral serves to rapidly absorb the excess of heat, in case the temperature of the room comes too near to the temperature of the calorimeter. The expansion of the column of mercury in *Th* appeared to be about 0.5 mm. for 0°.001 C. temperature-difference. In this way it was possible to keep the temperature of the calorimeter-water *L*, — also in the case of prolongated experiments, — constant within 0°.001 C., provided the water-bearing cover *D* is simultaneously made use of. This cover has been made of zinc-plate ; the top is provided with an air-thight tap, which

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current of R_2, which comes from A_1, is closed. In this case the current-circuit in which R_3 is inserted, is interrupted, which relay is connected with the municipal current (220 Volt). Owing to this, W_2 is short-circuited, so that the current which runs in the auxiliary-heating-spirals *S*, is now increased. If, however, the temperature of the water rise above 20° C., the thermo-regulator *Th* will cause the circuit of A_3 to be closed. The current in it is stronger now than that of A_2, and of opposed direction. This causes the relay R_1 to turn to the left, thus making currentless the circuit in which R_2 is inserted. Through this, the contacts are now closed for the circuit containing R_3; the resistance W_2 which was short-circuited before, is now switched on again in the circuit of the heating-current, the latter now being diminished; etc. etc.

can be shut hermetically, and with a screw-lock G provided with a glass window g. By means of the thick felt-layer only, small irregularities in the cooling-process of the calorimeter could not be prevented, even if the room-temperature was kept constant. Therefore this cover was provided with a number of nickel heating-spirals w'', surrounded by protecting-tubes, and with a number of partitions, in order to force the circulating water to flow in helical tracks within the cover.

Besides the porcelain tube B, which serves as a feeding-tube for the introduction of objects into the calorimeter and a tube on one of the sides as a passage for the third stirrer, the cover has only at the bottom the passages in which the tubes b and b' are tight soldered. Through these tubes the water in the cover communicates with that in the vessel J; so both tubes reach beneath the surface of the water. The cover is filled by opening K and by connecting it with a suction-pump; then K is shut again and the third stirrer W' is set in motion, by which the water is forced from the cover into the thermostat and then flows again in b. When all precautions are taken, a difference of temperature between the water L and that in the cover can no longer be perceived; so that also in upward direction the insulation of the calorimeter with respect to its surrounding, is complete. The wooden disk W' of the third stirrer is not directly connected to the brass-tube b', but to a much wider tube x, which is shut off at the bottom by a plate provided with little holes. This plate is fastened to the stirrer-shaft, by means of which the space between the cover and the thermostat is closed watertight, without the help of any ground-in connections. At a some space is left between L and the cover, in order to have a passage for the wires of the thermo-elements; etc. When experimenting, a, just as the whole calorimeter, is covered with a layer of felt 4 cms. thick.

§ 3. In the space of constant temperature described above there is the calorimeter proper. A big DEWAR-vessel H is, by means of a strong net of silk, suspended in a cylinder-shaped vessel Z. This vessel Z is 70 cms. high, has been loaded at the bottom with a thick layer of lead, and is shut off at the top by a ring E of hard wood, saturated with molten paraffine, and by a ditto cover C. The double-walled glass vessel is 42 cms. high and 11.5 cms. wide, and the walls have been silver-plated on both sides [1]). Between the wall Z and the DEWAR-vessel H there remains a thin layer of air; in the vessel and separated from it by a thin layer of felt v, is the calorimeter-body proper, viz. a cylindric block of pure aluminium A, weighing about 6000 grammes, and 27 cms. high, suspended by three strong silk wires, which just as the silk net y are fastened to the wooden

[1]) This beautiful DEWAR-vessel was made at the Physical Laboratory of the Leyden University; for the gracious assistance we wish to express once more our heart-felt thanks to the Directorium of said Institution.

ring E and which are kept together near the margin of H by a wooden ring r The aluminium block A, which has a diameter of 10.1 cms., possesses 38 cylindrical borings, arranged in two concentric circles, each of which is 16 cms. deep and 0.4 cm. wide. These borings serve to fix 36 thermo-elements of copper-constantan, arranged in four series of 9. These series can, at will, be connected parallel or in series. When standardizing these thermo-elements, the other two borings are used to fix two standard-thermo-elements ; or to control by means of two supplementary sets of thermo-elements which are arranged in series, any accidentally occurring, extremely slight fluctuations in the temperature of the calorimeter-water during the measurements. The arrangement of the borings is clearly visible in Fig. 4,

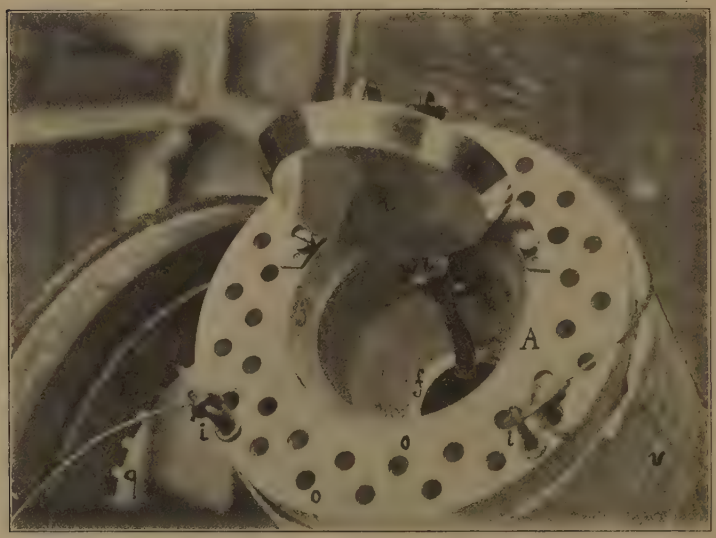

Fig. 4.

representing the aluminium-block seen from the top. In each boring there is a very thin-walled capillary tube o of porcelain at the bottom and fixed in the boring by means of closed ROSE's alloy, so that there exists an immediate metallic contact between the capillary and the aluminium-block. In these capillaries are the wires of the thermo-elements with their junctions in λ, which wires are covered with a layer of a well-isolating varnish and fastened to the bottom by means of shellac. Beforehand they have, over their entire length, been made properly homogeneous by repeated heating and cooling and further treatment according to WHITE [1]). The wires $h'h$ of the thermo-elements, which come from the calorimeter, are also well-

[1]) W. P. WHITE, Phys. Zeits., **8**, 337, (1907).

isolated. On leaving the DEWAR-vessel, they are led through the openings g of the wooden ring E, which are filled inside with a mixture of wax and resin. Giving any kink to the wires should be carefully guarded against. Outside the ring these wires rested originally on pieces of mica, placed on a flat-conical ring s'', which had been made of perforated zinc-plate. Later on, however, it was found that it was even better not to use the ring at all. The second junctions ξ of the thermo-elements are placed in a red-copper ring N below the water-level of the thermostat, this ring having a diameter of about 34 cms. It has been made of rectangular bar-copper of 1.3 cm. by 1.9 cm. These junctions are also placed inside thin-walled porcelain capillaries β, which by means of ROSE's alloy ε, have been sealed in 36 of the 38 borings of the red-copper ring N. When, as has been said above, the two other borings were used to control the temperature of the water, a series of thermo-elements were joined to them, whose other junctions had been placed in a DEWAR-vessel filled with pure ice. The copper ring N lies on the bottom of a hollow conical vessel γ of copper-plate, which has been filled almost to the brim with pure, molten and again solidified paraffine P. In order to maintain a perfectly constant temperature, it proved necessary to surround this jacket γ with a cylinder-shaped copper jacket F of the shape indicated in Fig. 1, and to add to it a screen π. It is better still to place a second copper screen outside the jacket F.

§ 4. The following remarks must be made about the temperature measurements by means of the thermo-elements. As is always done in this laboratory [1]), all measurements were made with the aid of a potentiometer-installation void of thermo-electric contact-potentials (made by O. WOLFF), this time with five in stead of the usual three decades ; potential differences smaller than those indicated by the smallest decade-unit, were measured by the deflections of a calibrated galvanometer (according to ZERNIKE), which, at a critical resistance of 30 Ohm and a sensibility of 10^{-10} Amp., had a period of only 2 seconds. The working current of the potentiometer was chosen in such a way that each unit of the compensator corresponded to 2000 Mikrovolt ; in the final measurements the deflections of the galvanometer were always measured both to the right and to the left, by means of a switch equally free from all contact-potentials, which allowed to reverse the direction of the current in the compensator at any moment. A very weak current always circulated in the bank, so that no measurements were begun, before there was absolute certainty, that the temperature of the resistance-coils did not undergo any change worth mentioning. Before each measurement, the complete compensation of the instrument was always controlled once more [2]).

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[1]) F. M. JAEGER, *Eine Anleitung zur Ausf. exakter physiko-chem. Messungen* (1913) Groningen, p. 14.

[2]) On moist days it appeared desirable, to blow a slow current of carefully dried air through the box of the potentiometer, in order to eliminate the condensed water-vapour on the coils.

The four couples of wires of the four series of thermo-elements, which had to serve as connections to the potentiometer were, well-isolated, led outside the calorimeter through the opening *a* and fixed side by side in a reservoir filled with solidified paraffine. They were then placed over glass-rods provided with mica-rings and in this way connected with the measuring-apparatus. The same compensator was also used, when measuring the furnace-temperature by means of a platinum-platinum-rhodium-thermo-element. It thus became necessary to put all measuring-instruments on inter- and terrestrial-connected metal-plates, as suggested by WHITE [1]), in order to prevent, when using electric resistance-furnaces, that at high temperatures, any leakage of the furnace-current to the measuring-apparatus could occur.

All temperatures have been reduced to the scale of the nitrogengas-thermometer of *Washington*, as fixed by DAY and SOSMAN. The platinum-platinum-rhodium-thermo-elements used were calibrated by comparison with a standard-element, which was standardized in *Washington*, and by determining a series of characteristic and well known melting-points [2]). For the alternate reading of the thermo-elements in the calorimeter and in the furnace, plug switches free from all contact potentials were constructed. Also for the connection in series or parallel to each other of the four groups of thermo-elements in the calorimeter, plug-contacts were used, which too were practically free from contact-potentials and accessory resistances. Besides, any disturbances of this nature could always be eliminated by the application of the method mentioned above, viz. of reversing the working current in the compensator.

The calibration of the copper-constantan-thermo-elements in series of nine elements, led in the first place to this result, that all elements appeared to be identical and to be fixed in the calorimeter with a complete insulation. For each set of 9 elements, it appeared that the temperature t as a function of the electromotive force E could be expressed by the equation: t (in degrees C) $= 0.00279698\ E - 0.00000000629\ E^2$, when E is expressed in Microvolts. From this it follows, that a potential difference of one Microvolt corresponds between 19 and 23° C., — that is within the limits of the temperature-variations of the calorimeter, which lie between 7000 to 8000 Microvolts in all measurements, — to a change of temperature of 0°.002703 C. for each set of thermo-elements. If all elements are connected in series, the indication of the 36 thermo-elements corresponds consequently to 0°.000676 C. for a potential difference of one Microvolt. Thus it appeared possible to determine temperature-differences of 0°.0001 C. still with absolute certainty.

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[1]) W. P. WHITE, Phys. Rev., (2) **8**, 337, (1907).

[2]) $NaNO_3$ (308°); $NaCl$ (800°); Li_2SiO_3 (1201°); artificial *Diopside* (1391°); artificial *Anorthite*; (1551°); $BaSiO_3$ (1604°) were used. Corrections of thermo-element K: at 308°: + 10 M.V.; at 800°: —13 M.V.; at 1201°: + 6 M.V.; at 1391°: + 23 M.V.; at 1604°: + 56 M.V.

§ 5. In the centre of the aluminium block *A* an opening 5 cms. wide was bored which continues with a gradually reduced diameter to a cylindrical boring *ϱ* of a diameter of about 2.7 cms. At the lower side of it a nicely fitting piece of aluminium *k* is fixed which firmly impinges on the walls and which has been provided with a steep conical boring. The whole inner-wall of this central channel, and also that of the conical part in its lower end is provided with a lining of purest platinum of 0.35 mm., the turned down and flattened border of which can be clearly distinguished in Fig. 4. This platinum-lining has a weight of about 120 grammes. By applying this conically narrowed part *k*, a much better contact is brought about between the calorimeter-wall and the introduced heated object, than with the original apparatus in which the object was caught on a platinum sheet, supported by a tungsten-spiral. The time necessary to restore the normal decrease of temperature of the calorimeter since the moment of introducing the heated object into it, could be reduced in this way from several hours to half an hour, while the maximum temperature, e.g. even in the case of platinum heated at 1600° C., appeared now already to be attained in about eight seconds, instead of after several minutes. By constructing a new and better-fitting platinum-lining of the calorimeter-space, it was finally possible to improve the interchange of heat to such a degree, that the total delivery of the heat of the hot object, — in the case that this is a metal [1]), — appeared to be completed *after a few seconds* already; so that it was not even possible to persecute the initial increase of temperature until its maximum by means of the switch gear of the potentiometer.

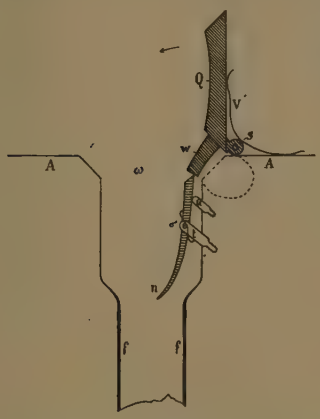

Fig. 5.

The heated object which falls into the openig *ω* of the metal-block is first caught by an extremely mobile trigger *n*, which enables the nickel lid *Q*, — which in its turn is driven, as indicated in Fig. 5, by the strong steel spring *V'*, — to shut off the opening *ω* in a minimum of time. This mechanism, which works like a "mouse-trap", and the lid *Q* are clearly visible also in Fig. 4.

Finally it should be stated that the porcelain tube *B*, which also passes the water-cover *D*, is firmly fixed in the wooden lid *C*, by which the cylinder of the calorimeter is closed at the top. This tube *B* forms the passage for the heated object into the channel of the calorimeter.

§ 6. For heating the substances to be tested, electrical resistance-

[1]) In the case of such substances as *water*, *porcelain*, etc. the complete heat-delivery lasts somewhat longer.

furnaces are applied with platinum-coils wound on their inside walls, of the type always used in this laboratory [1]).

In order to prevent as much as possible the heat-radiation from the furnace to the felt-jacket and outwards, the furnaces around and at their-bottom are provided with double-walled, detachable jackets and water-screens, in which a current of cold water is continually flowing (Fig. 6). The construction of these furnaces is indicated in Fig. 6. The furnace has

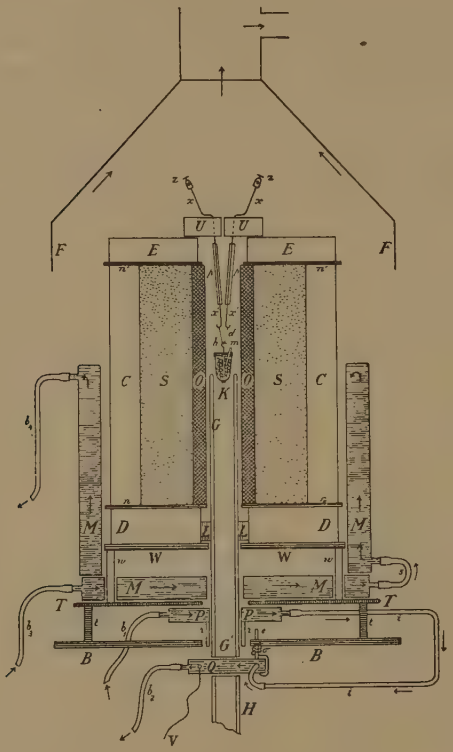

Fig. 6.

been placed on an iron frame W, which rests with three legs w on the iron table T, which in its turn stands with its legs t on the firm foundation-plate B. This last one can be moved on iron rollers over a couple of rails. The water-jackets, which are all interconnected, are indicated by M in Fig. 6. The furnace $U\,E\,C\,D$ which is composed of chamotte-parts and which is kept together by iron rings n and n' and by draw-bars (not indicated), has a core O of hard magnesite with a platinum coil of 1.3 mm. wire-diameter

[1]) F. M. JAEGER, *Anleitung*, etc., Groningen, (1913), p. 37).

wound on its interior wall; the filling *s* consists of burned magnesia. The MARQUARDT-tube *GG'* is, at the bottom, surrounded by the water-screen *P*, and is pressed against the tube by an elastic metal-tube *r*. A water-screen *Q* shuts off the tube at the bottom. This screen can be turned on a hinge *e* provided with a steel spiral string *o*; it can at the desired moment, — i.e. when the crucible is detached from its suspension-wire in the furnace, — be drawn aside by the pull-rope *V*, and then, within a very short fraction of a second, immediately be brought in its former position. *H* is the tube leading into the calorimeter. The cooling by *P* and *Q* is so effective, that the outgoing water in b_2 remains *perfectly cold*; and there is no appreciable radiation to the calorimeter possible, even when the furnace is brought at 1625° C. [1]). The chamotte-ring *U* consists of two parts, which enables the exact centring of the suspended system *xpx'K* in the furnace at any temperature. The still remaining, but very feeble currents of hot air, rising along the furnace-walls, were rapidly made harmless by letting them out with the help of a big ventilation-flap. In order to prevent an undesired heating of the room by the JOULE's heat of the furnace-current, the furnace-rheostat was also completely surrounded with a jacket of wood, and the heated air in it was, in a similar manner, finally eliminated along a range of pipes. Besides, great care was taken to keep the temperature of the room as much as possible constant at 20° C. day and night, after the central heating of the building had been partly turned off. This was done by means of a gas-oven, which had been provided with a big thermoregulator. The resistance-furnace had been mounted on detachable iron rails over the calorimeter; and from its remote station under the ventilator-flap, it could at the desired moment and with one single grip, be rapidly and perfectly be brought over tube *B* in the right position and as rapidly be removed to its original position.

In the course of the measurements it appeared however, that the furnace need not be removed, because of the very perfect insulation of the furnace and of the calorimeter; so that it now remains in its place after the necessary precautions have been taken.

The objects were suspended by a thin platinum wire in a platinum vessel (description see below) in the furnace, within its space of constant temperature; this platinum wire was instantaneously melted through by a strong electric current at the moment the object was dropped into the calorimeter. According to the nature of the substances to be investigated, occasionnally it proved necessary to construct, within the platinum-vessel, a lining consisting of a smaller vessel of hard porcelain. With a view to this, both the specific heat of the hard porcelain and that of the platinum had to be determined accurately. When describing the measurements, we shall, when necessary, refer to this arrangement of the experiment.

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[1]) This may be controled by variation of the time of falling of the heated object; usually this time did not exceed 0.05 till 0.1 second.

To determine the water-equivalent of the calorimeter and to standardize the thermocouples, a double-walled copper air-bath was used, which had been well-isolated with asbestos and felt, and in which, by means of electric heating, water-vapour of a temperature given by the momentary atmospheric pressure, was produced. Only after about three quarters of an hour it appeared that the object in it had entirely adopted the temperature of the air-bath, which temperature was determined by means of a thermo-element, which either touches the platinum-vessel or is placed into its centre. Also this heating-apparatus worked most satisfactorily, if the necessary precautions be taken.

§ 7. *Water-equivalent of the calorimeter: way of determining this value and of the coolingconstant k of the instrument.*

After the normal temperature-course of the calorimeter has been determined, and after the heated object has been introduced into the calorimeter at the moment τ_0, the temperature will first rise rapidly; then it will fall again, after which, when all the heat has been given out, the normal cooling-course of the calorimeter is at last re-established. When a calorimeter is used containing a liquid, by means of which a very rapid delivery of the heat and an equal distribution of it is effected by permanent intensive stirring, the temperature X at the moment τ_0, which the calorimeter would have attained at an *infinitely rapid* heat-exchange between the hot object, and the instrument, can, in a well-known manner, be found by a simple graphic extra-polation of the cooling-curve in function of the time. In the metal-calorimeter, in which this stirring is *not* possible, a maximum temperature C will be attained after a short time, which is dependent on the heat-conductivity of the metal, on the place in the metal-block where the thermo-elements have been located, and on other factors. The curve which gives the temperature T as function of the time τ (Fig. 7) can be thought as existing of two parts: the "normal" part DE and the "abnor-

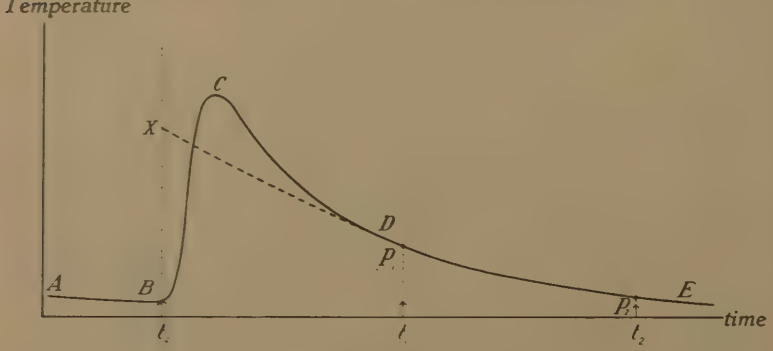

Fig. 7.

mal" part $B\,C\,D$. If the temperature-course of the calorimeter before the introduction of the heated object is represented by $A\,B$, the question is to substitute for this abnormal part the "normal" curve P_1X, which must be considered as the piece of the normal cooling-curve adjoining $D\,E$. In this case X represents the required value of the calorimeter-temperature at the moment τ_0, which would have prevailed in the calorimeter at an infinitely rapid exchange of the heat and at an infinitely rapid indication of the temperature by the thermocouples, as a mere consequence of the heat emitted by the heated object. As the thermo-elements have been fixed about half-way between ω and the outer-wall of the metal-block, the maximal temperature C is always higher here, than the true temperature X.

According to a method of MAGNUS, which is somewhat extended by us, this temperature X can be found by means of the following considerations.

If it be supposed, — which suppositions may be considered as very probable ones, — that :

1st. also during long intervals of time the mean value of the temperature of the water surrounding the calorimeter remains constant ;

2nd. the loss of heat of the calorimeter as a whole is dependent *solely* on the difference in temperature at any moment between the calorimeter and the surrounding water, this loss of heat being always directly proportional to that difference of temperature ;

than, if e is the electromotive force of the thermo-couples and τ the time, we have :

$$-\frac{\partial e}{\partial \tau} = k \,.\, e.$$

If at the time $\tau = 0$, the heated object is introduced into the calorimeter, it follows that :

$$-\int_0^{\tau} \frac{\partial e}{e} = k \,.\, \tau.$$

Therefore :

$$^{10}log\, e_0 - {}^{10}log\, e_\tau = 0{,}4343 \,.\, k \,.\, \tau,$$

e_0 being the electromotive force of the thermo-elements at the time $\tau = 0$.

From this follows :

$$^{10}log\, e_0 = {}^{10}log\, e_\tau + 0{,}4343 \,.\, k \,.\, \tau = {}^{10}log\, e_\tau + k' \,.\, \tau.$$

To find the "cooling-constant" $k' = 0.4343.\ k$ of the calorimeter, we have measured the electromotive forces e_{τ_1} and e_{τ_2} at the moments τ_1 and τ_2, after the cooling-course of the instrument had again become "normal", i.e. in Fig. 7 after the point D has been passed.

From :

$$-\int_{\tau_1}^{\tau_2} \frac{\partial e}{e} = \int_{\tau_1}^{\tau_2} k \,.\, d\tau$$

it follows :

$$k' = 0{,}4343\, k = \frac{^{10}log\, e_{\tau_1} - {}^{10}log\, e_{\tau_2}}{(\tau_2 - \tau_1)} .$$

In this way we found in five series of preliminary experiments, which were extended on intervals ranging from 16 to 20 hours, for k' the consecutive values : 0.0006746 ; 0.0006744 ; 0.0006742 ; 0.0006741 ; and 0.0006742 M.V. pro minute. Hence, it is seen that with this arrangement of the apparatus, even during very long intervals of time, k' may indeed be considered as being practically *constant*, having the mean value : 0.0006743 M.V. pro minute. Afterwards, when all necessary improvements of the apparatus were made, in order to eliminate all eventually occurring differences of temperature between the water in the cover and in the vessel *J*, the value of k' appeared to be somewhat greater, being about 0.000702 M.V. pro minute.

Moreover, the value of k' was redetermined in each measurement by measuring the electromotive forces e_{τ_1} and e_{τ_2} with an interval of 10 minutes since the moment at which the normal course of the calorimeter was re-established.

As an illustration of the way in which for instance the water-equivalent W of the calorimeter was determined, the following data may be mentioned here, which were determined before the final improved platinum-lining of the instrument was applied.

Into a small conical crucible of platinum, accurately fitting in the conical boring k of the calorimeter, a sufficient and exactly known quantity of pure water was introduced. The crucible was closed by means of a platinum cover, tightly soldered to it with silver ; a small platinum tube for filling the crucible, as well a small hooklet were fixed in this cover.

Weight of the platinum : 10.8192 grammes ; *weight of the silver :* 0.0562 grammes ; *weight of the tin :* 0.1408 grammes ; *weight of the water :* 5.9564 grammes.

The water-equivalent of the whole crucible was, therefore, equal to : (10.8192 $\times$ 0.032 + 0.0562 $\times$ 0.055 + 0.1408 $\times$ 0.044 + 5.9564) = = 6.3125 calories [1]) pro degree C. The crucible was suspended in the copper air-bath formely described, by means of a thin wire ; then it was heated by means of water-vapour and, after the temperature had become quite constant, it was suddenly detached by means of a special mechanism and caught in the calorimeter, the temperature being now observed after regular intervals of time.

Reduced barometer-indication : 762.66 mm. (0° C.) ; the boiling point of the water is, therefore, equal to : 100°.096 C. The temperature of the crucible read directly was : 100°.07 + 0°.03 (correction for the projecting mercury-thread) = 100°10 C.

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[1]) Here and in the following we have adopted as unit always the *mean gramme-calorie* ; the reduction of this unit to the other usual units is, moreover, in each case easily made.

The temperature of the surrounding water was: 20°.067 C.

(In the following table the electromotive forces of the thermo-couples are indicated by e'; they must be multiplied by 2000, if these values be reduced to Microvolts).

Time:	Electromotive Forces observed:		
	e' (to the right):	e' (to the left):	
P.M. 1h 59½m	0.0498	—	
2h 0m	—	0.0496	
2h 0½m	0.0498	—	
2h 4½m	—	0.0496	
2h 5m	0.0499	—	Mean value 0.04975.
2h 5½m	—	0.0496	
2h 9½m	0.0499	—	
2h 10m	—	0.0496	
2h 10½m	0.0499	—	
2h 11m	← The crucible is introduced into the calorimeter		
2h 15m	—	0.2729	
2h 20m	0.3068 (max.)	—	
2h 25m	—	0.3046	
2h 30m	0.3010	—	
2h 35m	—	0.2976	
2h 39½m	0.2952	—	
2h 40m	—	0.2947	
2h 40½m	0.2946	—	
2h 44½m	—	0.2924	
2h 45m	0.2923	—	Mean value: 0.2923.
2h 45½m	—	0.2919	
(After 19 hours):			
A. M. 9h 44½m	0.0465	—	
9h 45m	—	0.0461	Mean value: 0.0463.
9h 45½m	0.0465	—	

From the values of e': 0.2923 and 0.0463, the value of k', that of the temperature X at $2^h\ 11^m$, and finally the value W of the water-equivalent, are calculated in the following way:

Calculation of k'. The values of e' mentioned above correspond to the electromotive forces e_{τ_1} and e_{τ_2} of 584.6 M.V. and 92.6 M.V. respectively, $(\tau_2 - \tau_1)$ being here: 1140 minutes. From these data follows: $k' = 0.0007020$ M.V. per minute.

To find e_{τ_0} from $e_{\tau_1} = 584.6$ M.V., it must be remembered that between both moments 34 minutes have elapsed; to find the *increase* of temperature at the moment τ_0, it must be borne in mind, that the temperature of the calorimeter at $2^h\ 11^m$ was 99.5 M.V. above that of the surrounding water (20°.067 C.).

Therefore, we have: $log\ e_{\tau_0} = log\ 584.6 + 34 . k' = 2.76686 + 0.02387 = 2.79073$; thus $e_{\tau_0} = 617.3$ M.V., this value corresponding to: $617.3 \times 0°.000676$ C. $= 0°.4175$ C. The temperature of the calorimeter at τ_0 was, therefore, equal to: 20°.4845 C.; while the *increase* of the temperature of the instrument was: $(617.3 - 99.5) \times 0°.000676 = 517.8 \times 0°.000676 = 0°.3503$ C.

The platinum crucible, consequently, has suffered a decrease of temperature from 100°.096 C. till 20°.4845 C. corresponding to a delivery of heat of: 79.6115×6.3125 calories $= 502.547$ calories. As the *increase* of temperature of the instrument, caused by this heat-emission, was: 0°.3503 C., the water-equivalent W of the calorimeter is, therefore, calculated to be: 502.575 : 0.3503 calories, i.e.: 1435.1 calories.

In a series of experiments of this kind, made with the finally perfectionated instrument, values for the water-equivalent W were determined, which did not differ from each other more than 0.07 %. The improvements applied to the water-cover were made to completely fulfill the condition mentioned above sub 2nd, any oscillations of temperature, even very small ones, now being thoroughly eliminated. After the aluminium-cone k and the new platinum-lining were also applied in the channel of the calorimeter, the renewed measurements of W furnished, in seven series of experiments, consecutively the following data: 1417.2; 1417.9; 1418.7; 1417.0; 1417.9; 1417.8; and 1418.8 calories.

The mean value of these is:

$$W = 1417.9 \pm 0.9 \text{ calories.}$$

The deviations are not greater than $\pm$ 0.063 %; which is an accuracy more than sufficient. The number mentioned was, therefore, used by us in all later measurements.

The apparatus here described, which is in use now already for a long time, has given excellent results in all respects. In the next paper we will publish some of these results.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Astronomy. — *Preliminary Report on the Expedition to Lapland for the Observation of the Total Solar Eclipse of June 29th 1927.* By A. PANNEKOEK and M. G. J. MINNAERT.

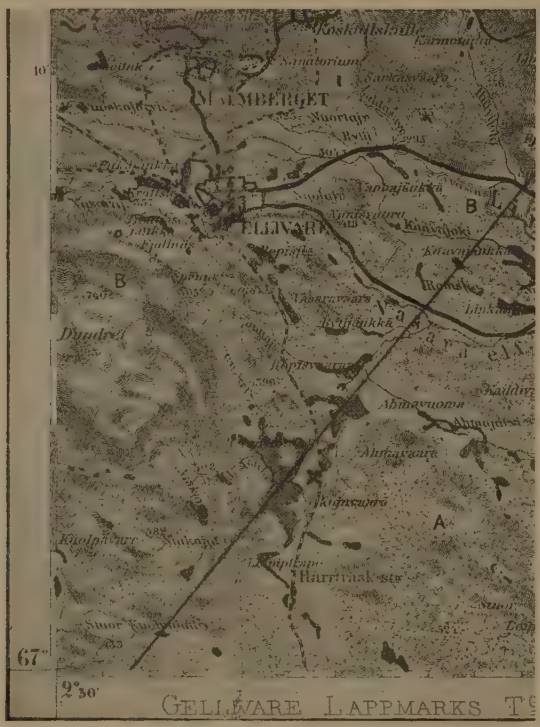
(Communicated at the meeting of September 28, 1927).

1. The observation of the total solar eclipse of Jan. 14, 1926 at Palembang having failed through clouds, it was to be feared that in the much more favourable eclipse of 1929 our instruments should have to be used, before by practical experience possible faults could have been detected and corrected. This consideration induced the Eclipse Committee to organize an expedition for observing the total eclipse of June 29th 1927. As the zone of totality traversed England, the South of Norway and the North of Sweden a limited programme could be executed at moderate expense. By the short duration of the eclipse study of the spectrum of the corona would be difficult, but for the observation of the flash a test of the Cooke spectrograph was quite possible. For this reason a request was made to the "Hollandsche Maatschappij van Wetenschappen" at Harlem to destine the "PIETER LANGERHUIZEN fund" for this year for an expedition to observe this eclipse. In its session of May 15th 1927 the Society decided to comply with our request. Immediately the preparation of the expedition, for which preliminary experiments had been made already at the Heliophysical Institute of the Utrecht Physical Laboratory, was taken energetically in hand.

As our place of observation Gällivare in the northern part of Sweden was chosen, chiefly on account of the greater height of the sun (28°, while it was 22° at Aal in Norway), and also, because for our instrumental outfit the vicinity of the technical resources of a large industrial plant was desirable. The instruments which were to accompany us, were the large Cooke spectrograph with moving lens, and the coronacamera with liquid prism. The financial means available allowed to send out only three observers, Messrs A. PANNEKOEK, M. G. J. MINNAERT and N. W. DOORN, the latter assistant at the Leyden Observatory. By special funds Mr. W. BLEEKER, of the Utrecht Physical Laboratory, was enabled to join the expedition; his wireless apparatus enabled us to compare our chronometers directly with the wireless time signals.

The members of the expedition left on May 26 and arrived at Gällivare on June 1. The same day an observing site was selected and the building of piers and of a shed was begun. The instruments, which had been sent by ship to Stockholm and further by rail, reached our camp on June 13, and their erection was begun immediately.

2. *Observing site.* Most expeditions to Lapland chose their sites in the immediate vicinity of the small towns of Gällivare or Malmberget, at a distance of 7—9 km from the central line. For our work it was necessary to have our observing station in the immediate neighbourhood of the central line; on the accompanying map the central line is drawn and the observing place chosen



is indicated by a cross. The central line has been computed from the elements of the Nautical Almanac, to which corrections $dx = -0.00060$ and $dy = +0.00003$ were applied, communicated to us by Mr. L. J. COMRIE, Deputy Superintendent of the Nautical Almanac Office. The geographical coordinates of our observing site, taken from the map, are

$$\lambda = 1^h\,22^m\,58^s\,\text{E.} \quad \beta = +67°\,3'.5\,;$$

it is situated some kms North of the wayside station Harrträsk of the electrical railway Narvik—Luleå. For this site the moments of 2^d and 3^d contact were computed 5^h 46^m 6^s.8 and 5^h 46^m 48.^{s}4 G.M.T., thus giving the duration 41.6 seconds. The points of contact on the solar limb were situated 2° 1′ below the diameter inclined 7° 10′ to the daily motion.

Our camp could only be reached by railway; without the aid of the State Railway Authorities, who ordered four trains to stop there each day,

our work would not have been possible. They also had our camp connected with the 4000 Volt cable running along the railway ; the alternating current was transformed down to 220 Volt ; it served so for illumination in our dark room and, converted to continuous current of 200 Volt by means of a motor and dynamo, was used for charging a battery of storage cells and for feeding an iron arc. The storage cells, also put at our disposal by the Railway Authorities, drove the motors for the moving lens and for the rotating cylinder of the Cooke spectrograph. We are indebted for the loan of the necessary instruments for electrical measurements to the Laboratory of the " Technische Hoogeschool" at Delft.

3. *Adjustment of the instruments.* In the report on the Sumatra expedition the mounting of the Cooke spectrograph has been described. To reflect the sun beams horizontally in such a way that the daily motion of the solar image would be horizontal, reflection by two mirrors was necessary then. The first, a coelostat mirror parallel to the earth's axis, reflected the solar image to a point of the meridian with opposite declination ; the second mirror then reflected it to the southpoint of the horizon. As, however, for the eclipse of 1927 the sun's declination was $+23° 17'$ and the latitude $67° 3'$, one reflection on a coelostat mirror threw the image to a point $20'$ below the southern horizon ; hence one mirror sufficed here. The adjustment of the mirror was made in the same way as described in the former report, by means of the same two altazimuths from Delft and Wageningen, once more kindly lent us by Prof. SCHERMERHORN and Prof. DIEPERINK. The adjustment was more difficult here than in the Indias, because the azimuth of the polar axis and the inclination of the mirror to the axis are interdependent with a factor $\sin \beta$. For the azimuth pointings we could make use of a landmark on the top of the Dundret, 7 km distant, for which an azimuth $136° 34'$ was found from observations of the sun.

The reflected sunbeams were collected by the Steinheil objective of the Utrecht Observatory into a solar image of 3 cms on the slit plate. This objective was moved by a motor with clock regulation ; its velocity was regulated the preceding days so that on the eclipse day the daily motion was exactly compensated. The slit was set perpendicular to the relative movement of the moon, hence it was inclined 7° to the vertical, and in the same way the prism train, which was traversed twice by the light, and the spectrum in the focal plane were inclined 7°. The prisms were set at minimum deviation for λ 4380 ; the spectrum extended from λ 4150 to λ 4700, but the extreme wave-lengths were not exactly in focus. For the first flash the slit cut an arc of 8° of the sun's limb ; in this position also the exposure for the corona spectrum was made, and then the mirror, by means of a lever between two pins, was turned through a small angle to bring the place of 3^d contact upon the slit. The distance of the pins had to be regulated accurately the preceding days ; but through lack of sunshine this could not be performed wholly satisfactorily.

In order to throw the sunlight into the coronacamera we could, by the kindness of Prof. R. SCHORR, make use of a coelostat of the Hamburg Observatory, provided with our 20 cm mirror, and adapted to this high latitude. The mirror was placed at a distance of 6 m. North of the liquid prism ; the adjustment was made in the same way as for the other instrument. This large distance was chosen in order that only the immediate surroundings of the sun could send light into the camera ; by surrounding the mirror and the light path with black screens, also other spurious light was excluded. The liquid prism, with its refracting edge set horizontally, was packed tightly in cotton wool to prevent any variation of temperature. To get the whole spectrum an ordinary and a panchromatic plate (Lumière Opta 68 × 59 mm, and Ilford Panchromatic 68 × 40) were put into the plate holder beside each other in such a way that the division fell between λ 4900 and λ 5000. On this double plate two exposures were made, a short one of 3 sec. lasting from 5 to 8 seconds after the beginning of totality, and a longer one which should end 5 sec. before the end of totality ; between them the plate was displaced 33 mm. Then a second pair of plates was exposed 5 sec. to the solar crescent, weakened by an evenly blackened photographic plate.

The mirrors were resilvered some days before the eclipse.

The adjustment of the instruments was hampered very much by rains ; at the eclipse hour the sun was visible only on 5 days between June 13th and 27th. On June 28th began the Lapponian summer, a period of constant bright weather — often however with occasional clouds — with high temperature, which made the work increasingly difficult, especially by the increasing multitudes of gnats.

4. *The time service.* After the radiomasts had been erected the chronometers were compared regularly with the wireless time signals, for so far as the strong perturbations by the electric railway currents allowed this. The first days at 20^h G.M.T. a time signal from Djetskoe Selo was received ; afterwards we could hear at 12^h G.M.T. the signal of Nauen, transmitted by Stockholm and Boden. The last days, however, it was inaudible in our camp, and we were obliged to compare one of our chronometers at Gällivare with those of the German expedition. That Bordeaux had sent extra signals in the morning of the eclipse, but therefore omitted its regular signal at 7^h G.M.T., we learnt by chance only some days after the eclipse.

To know the moment of 2^d contact we made use of two methods described already in the Sumatra report. A telephone connection could be made at no shorter distance, because of the rough inaccessible ground between, than at Jokkmokk, 60 km to the S.W., at $\lambda\ 1^h\ 19^m\ 0^s$, $\beta + 66° 36'.1$, where the computed time of 2^d contact was $5^h\ 45^m\ 5^s.3$ G.M.T., 61.5 seconds ahead of the time at our site. We found Messrs WESTERLUND and VÄSTFELD, resp. surgeon and photographer at that

place, willing to observe the beginning of totality and give us a signal by telephone. The State Telegraph Authorities provided for a continuous connection of their observing place via Jokkmokk—Murjek—Gällivare with our camp every morning $5\frac{1}{2}$ to 6^h G.M.T. from June 25th to 29th. One observer was to watch the appearance of Bailey's beads or the disappearance of the sun, the other would observe the passage of the shadow over the country. The telephone connection worked well all those days.

The other method consisted in the projection of a solar image of 12 cm by means of a telescope of 8 cm aperture. The length of the chord of the crescent 20^s, 12^s, 8^s, 6^s before 2^d contact was computed 0.865, 0.778, 0.695, 0.635 diameters. On the screen lines were drawn at these distances parallel to the moon's motion. The projecting telescope was placed between the Hamburg coelostat and the liquid prism ; hence 5^s before 2^d contact it had to be removed by an assistant.

5. *The eclipse day.* The arrangement for the eclipse was :

Cooke spectrograph : Dr. M. G. J. MINNAERT, assisted by Mr. W. BLEEKER for the moving lens and the mirror ; coronacamera : Mr. N. W. DOORN ; time service Prof. A. PANNEKOEK, assisted by Magister J. L. H. MOOSBERG, teacher at Malmberget, who also during the preparations had given us valuable aid. Several rehearsals had taken place on the preceding days.

In the morning of June 29 the sky was nearly clear ; during the partial phase some thin clouds passed before the sun. During totality the sun was quite cloudless. On the projected image the sun's limb was seen strongly boiling.

The telephone signals from Jokkmokk were received $5^h\ 45^m\ 6$—7^s (observation of the sun) and $5^h\ 45^m\ 11$—12^s (observation of the shadow); probably in consequence of the small difference in diameter of the sun and the moon the decrease of illumination was not so sudden as in other eclipses. The 2^d contact was thus assumed to take place at $5^h\ 46^m\ 9^s$, and in this way the seconds —20s, —12, 11, 10 ..... were called out. The projected thin crescent — of which one cusp was broken up into separate specks — was somewhat too short, i.e. the counting was 1^s too late ; thus in counting the number 6 was omitted and the numbers 8, 7, 5, 4, 3, 2, 1, 0, 1, 2 ..... were called. The disappearance of the sun's light was not observed ; from the observations of the crescent $5^h\ 46^m\ 8^s$ G.M.T. was the time of 2^d contact. At 38 the place of 3^d contact was seen brightening, and after 40 the sunlight reappeared ; $5^h\ 46^m\ 48^s.5$ G.M.T. may be taken as the end of totality.

At the Cooke spectrograph the moving lens was started at $5^h\ 44^m\ 17^s$. In the finder 70 sec. before 2^d contact several Fraunhofer lines (H β and surroundings) were seen to be reversed. At count —5^s the circuit for the motor of the rotating cylinder was closed, and the first plate was exposed ; on account of the slipping of the driving cord the cylinder had to be

displaced at first by hand, so that a somewhat too long time elapsed before the second exposure. At count $+7^s$ the circuit was broken, the 6^{th} plate was exposed before the occulting sector stopped, and the 7^{th} plate was exposed for the coronal spectrum from $+17^s$ till $+34^s$, the moment that the mirror was turned. A faint orange ring was visible on the slitplate; the slit seemed to stand outside the moon's limb. The motor was again put into action between $+36^s$ and $+37^s$, and was stopped after the exposure of the 12^{th} plate.

With the coronacamera the first exposure lasted from $+5^s$ till $+8^s$, and after moving the plate, the second exposure was given from $+11^s$ till $+37^s$. Then the plateholder was changed and an exposure on the sun's crescent was made from $+18^s$ till $+28^s$.

6. *The comparison spectra.* Photographic negatives, which will be used for photometric purposes are standardized, as a rule, by putting comparison spectra of known intensity upon them. In our case these spectra, for fear of spurious light on the eclipse plates, were taken on other plates, which were cut from the same piece, and were developed together with the eclipse plates. The taking of these comparison spectra occupied us several days after the eclipse in increasingly difficult conditions.

For each of the 12 plates taken with the Cooke spectrograph 3 sister-plates were exposed: one to the solar spectrum, one to the spectrum of an iron arc, and one to the continuous spectrum of a Nitralamp of known temperature and distribution of energy along the spectrum. In all these cases the slit was equally illuminated by the source, and a reducer, consisting of a thin glassplate, half silvered in equal steps of decreasing transparency (Stufenfilter) was placed before the slit. By this means every comparison spectrum was divided into homogeneous strips, for which the relative intensities were exactly known.

For the plates taken with the coronacamera also two kinds of standardizing spectra have been taken on sister-plates; a broad slit with collimator was set before the liquid prism and illuminated one time by a Nitralamp shining on a piece of chalk, another time by a Neonlamp giving a series of monochromatic rectangles. Also in this case the stepped absorbing screen was set before the slit.

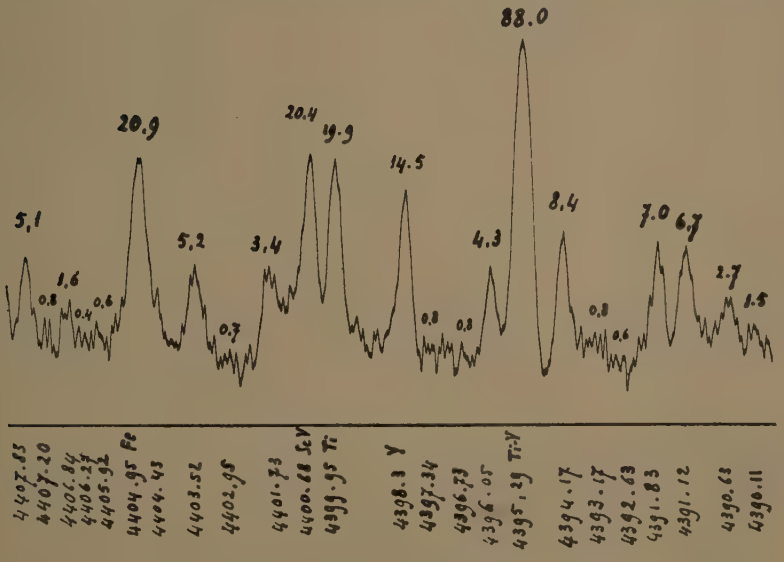
The plates were developed (always eclipse plates and sister plates together) by Messrs MINNAERT and DOORN; here unexpected difficulties arose by the tropical temperature in our dark room for nearly the whole 24 hours of the day. Therefore as a developer metol-hydrochinon-borax, which is of much use in the Indias, and which gives weak contrasts and little fog, was used. The panchromatic plates were at first desensitized in pinakryptol and then developed as ordinary plates. Distilled water was supplied by the laboratory of the Iron Works at Malmberget, which had also procured us nitric acid for silvering the mirrors.

After the plates had been developed the instruments were packed on

July 5th ; part of them, which was wanted for the observations on Gornergrat, Mr. MINNAERT took with him to Utrecht ; the rest was conveyed by the steamer "Wallrat Tham" from Luleå to Rotterdam.

7. *Results.* The first plate of the Cooke spectrograph shows the flashspectrum consisting of lines of nearly 3 mm, superposed on a somewhat narrower strip of continuous spectrum of the sun's border. Between λ 4150 and 4700, a number of 300 emission lines may roughly be estimated; on the continuous strip they are combined in a varying degree with absorption lines of the border. The next plates only contain, with decreasing intensity, some of the brightest chromospheric lines of H and He ; probably by the slow starting of the motor the 2d plate was exposed only after 2d contact. The 7th plate, which was exposed 17 seconds, does not show any coronal line. The other plates, which should have been exposed to the second flash, contain no lines ; probably the slit stood far beyond the sun's limb.

The first plate, part of which has been reproduced in fig. 1 of Plate I renders it possible, by means of the comparison spectra, to deduce values for the intensities of the chromosphere lines. As an instance of the procedure followed we give below for a small part of the plate, a registrogram made with a MOLL registering microphotometer ; the straight



lines at the top and the bottom of the figure denote black (transmission 0) and clear film. In the same way registrograms have been made from the

strips of the continuous comparison spectrum, from which the transmission was read for each strip of known intensity. This gives the relation between the transmission of the silver deposit and the intensity of the light for a number of values ; they were represented by a curve, which was used to deduce the intensities in the flash registrogram for the tops of the curve, rendering the emission lines, and the lowest points indicating the background ; by subtraction a value for the intensity of each line was found and has been inscribed in the figure. All lines in this part of the spectrum, contained in MITCHELL's large catalogue, are visible in our curve.

On the plate taken with the corona camera, (of which fig. 2 Table I shows a reproduction to scale) both exposures (of 3^s and of 26^s) contain a strong continuous spectrum, strongest of course in the tangential bands, and a number of monochromatic rings too. For the greater part they are chromospheric emissions ; they may be identified with the following lines :

3889 (Hζ), 3934 (Ca+), 3969 (Ca+, Hε), 4026 (He), 4078 (Sr+) 4102 (Hδ), 4216 (Sr+), 4341 (Hγ), 4472 (He), 4861 (Hβ), 5876 (He), 6563 (Hα).

Furthermore three coronal rings are visible at λ 6375, λ 5303 and λ 3987. In figs. 3 and 4 Plate I, a five times enlarged reproduction of parts of the exposure of 26 seconds, these rings are easily visible. Perhaps a trace of the emission λ 4231 is to be found on the negative, but quite uncertain. If we compare this with the intensities, given by STRATTON and DAVIDSON (for these lines 5, 20, 10, 10) then it follows that the 4231 emission in this eclipse was fainter than 1926 Jan. 14th and in other eclipses. This explains at the same time why the 7th Cooke plate does not show any coronal line. The small number of coronal rings on the corona camera plate is chiefly due to lack of contrast with the continuous background, which in this eclipse was very strong because the lowest and brightest parts of the inner corona were not covered by the moon. A still greater dispersion would have been needed to weaken the background so much that more rings could be visible. We will try, by measuring the blackness of the rings on this plate, to derive values for the intensity of the monochromatic light of the corona by means of the comparison spectra.

Acknowledgments. In concluding we wish to express our best thanks to all who have by their assistance contributed to the success of our expedition :

to the "Hollandsche Maatschappij van Wetenschappen" at Harlem, for granting the financial means, by which the expedition was made possible ;

to the Swedish State Railway Authorities, who gave a reduction of 50 % on the freight of the instruments to all expeditions, and who by many facilities made it possible for us to occupy a site near the central line ;

to the Swedish State Telegraph Authorities, who connected our camp with Gällivare by telephone, and provided for a direct telephonic connection with the Jokkmokk observers on the eclipse day ;

to the Luossavaara—Kirunavaara Aktiebolaget for technical help from

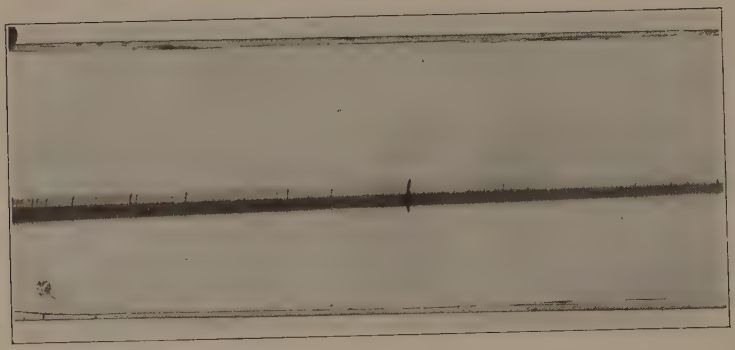


Fig. 1. Spectrum of Chromosphere (λ 4210 to λ 4530) photographed with the COOKE-spectrograph.

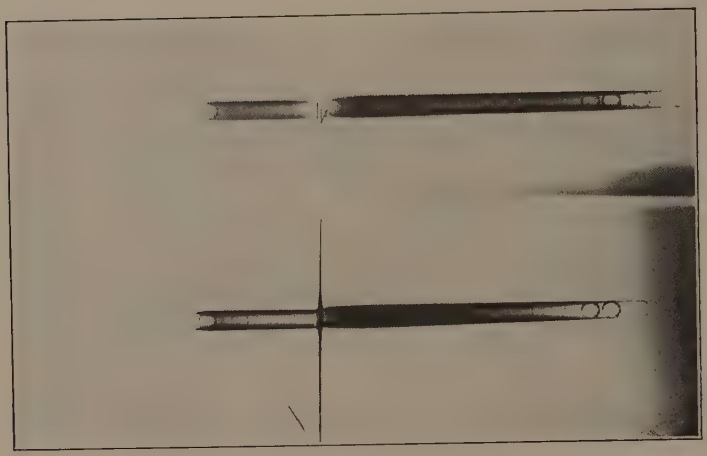


Fig. 2. Spectra of Chromosphere and Corona with the Corona Camera.

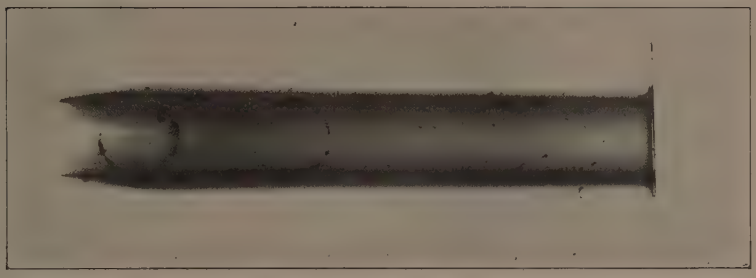


Fig. 3. Red, yellow and green part of Fig. 2 (enlarged 5 times).

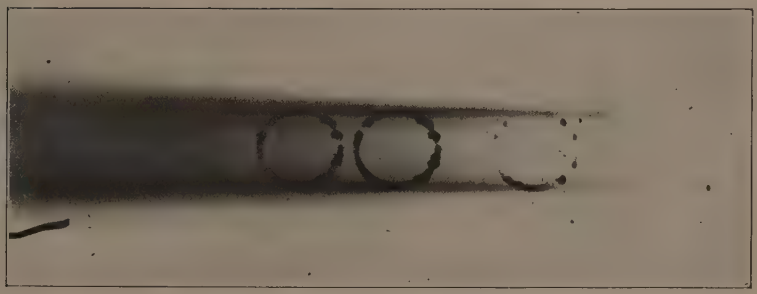


Fig. 4. Violet part of Fig. 2 (enlarged 5 times).

its Laboratory at Malmberget, and for free transport of the greater part of our instruments with one of its oreboats from Luleå to Rotterdam ;

further to the officials of the Gällivare railway station, especially to Herr Stationsinspektor AXEL FRIBERG, who with the greatest kindness was always ready to meet our wishes ; to Herr Electroingeniör G. SANDVALL at Kiruna, for valuable help in various ways, to Herr Telegrafkomissar LINDGREN at Gällivare ; to Magister J. L. H. MOOSBERG, who before and during the eclipse took part in our work as an assistant ; to Messrs WESTERLUND and VÄSTFELD, surgeon and photographer at Jokkmokk, for acting as observers at our telephone post, to Mr. C. NOOME, Director of the "Provinciale Utrechtsche Electriciteitsmaatschappij", who supplied us with a motor and dynamo for electric current ; to Mr. G. J. IMMINK, Dutch consul at Stockholm, who gave valuable information and help for the transport of our instruments.

Botany. — *On the retarding influence of the longitudinal component of gravity on the geotropic reaction of roots of Pisum sativum.* By WILLEMINA M. COELINGH. (Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of September 24, 1927).

The sine-law for geotropism states that when a force F (gravity or centrifugal force) makes an angle α with an orthotropical organ, its tropistic action is such, as if only the component perpendicular to that organ existed. The action is, therefore, proportional to $F \sin \alpha$.

However, it has been shown lately for roots that a force, acting in the direction of the axis of an organ, need not be without influence, it may e.g. change the speed of the tropistic reaction.

With main roots of Lupinus albus M. M. RISZ found that a longitudinal force checks a transversal geotropic stimulus.

W. ZIMMERMANN noticed that in main roots of Lepidium sativum an inverse longitudinal force (i.e. directed from top to base) slightly weakened a preceding transverse stimulus.

H. LUNDEGÅRDH experimented with Pisum. He saw in the longitudinal component one of the causes of the plagiotropical growth and of the constant angle made with the direction of gravity by the secondary roots of the first order. According to him a secondary root is orthotropical and does not assume a vertical position only because in the angle α the action of the transverse component ($mg \sin \alpha$) is wholly counteracted by the influence of the longitudinal component.

G. VON UBISCH repeated his experiments and extended them to main roots of peas. These roots are also supposed to show a constant equilibris-angle with the direction of gravity, though much smaller (about 5°) than that of the secondary roots (about 70°), the checking influence of the longitudinal force being much smaller in the main roots. Moreover she carried out quantitative experiments on the influence of the longitudinal force. She stimulated a secondary root both transversally and vertically, one of the forces being a centrifugal force, the other being gravity. She then determined the amount of centrifugal force required to keep the roots just straight. It appeared that this happened when the longitudinal force was about $^1/_3$ of the transverse force, so mg and 3 mg, or $^1/_3$ mg and mg. In this she sees a support of LUNDEGÅRDH's opinion (she found a constant angle of 70° and tg 70° is about 3).

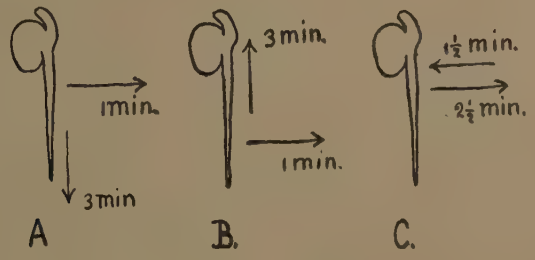
F. RAWITSCHER has pointed out that her experiments are not very convincing in this respect. The two forces she studied will have the same action as their resultant force and this resultant force makes an angle of about 70° with the root. Her experiments, therefore, only show that a secondary root is at rest even when it makes an angle equal to the constant angle with this resultant force, which is greater than *mg*. The same may be said of her experiments with main roots. RAWITSCHER suggests to let the two forces work intermittently with the aid of an intermittent clinostat.

I did this and for this purpose took the same race of peas as used by LUNDEGÅRDH and Miss VON UBISCH: the "grüne Concordiaerbse" which Dr. ÅKERMAN was kind enough to send us from Svalöf.

I soaked them for 12—24 hours, removed the seedcoat and fastened them by means of pins in glass culture dishes. The bottom was covered with paraffin on which a piece of wet black filter paper was placed. The roots did not touch the paper and, therefore, grew in moist air. Care was taken to ensure sufficient ventilation and the humidity was kept as high and as uniform as possible. In the dark room the temperature was usually 18—20° C.

The experiments were carried out with the aid of a new intermittent clinostat constructed in the botanical laboratory of the university of Utrecht and not as yet described. I also used an intermittent clinostat of FITTING.

I worked chiefly with main roots, about 3 centimeters long (about 3 days after germination). Each experiment was carried out with 3 dishes *A*, *B* and *C*, containing 8 peas each. The axis of the clinostat was horizontal, gravity acting alternately in the directions and during the periods indicated in the drawing.



Dish *A* and *B* were placed on the new clinostat, *C* on the one of FITTING. In this way I succeeded in stimulating all the peas transversally 1 minute in every 4 minutes. In the remaining 3 minutes the roots in *A* were stimulated longitudinally, those in *B* inverse-longitudinally; those in *C* received two equal and opposite transverse stimuli. Sometimes I stimulated all three dishes 2 minutes and 1 minute, namely in experiment 5 and 6, but this makes no real difference.

TABLE.

Number	A		B		C		Temperature in ° C.
	Shows asymmetry after:	Clearly bent after:	Shows asymmetry after:	Clearly bent after:	Shows asymmetry after:	Clearly bent after:	
1	1 h. 50 min.	∞	50 min.	1 h. 50 min.	50 min.	1 h. 50 min.	$19^1/_2$
2	3 h. 15 min.	∞	45 min.	3 h. 15 min.	45 min.	3 h. 15 min.	$19^1/_2$
3	1 h. 25 min.	3 h. 50 min.	50 min.	2 h. 35 min.	50 min.	2 h. 35 min.	$17^1/_2$
4	∞	∞	1 h. 5 min.	2 h. 35 min.	1 h. 5 min.	2 h. 35 min.	$17^1/_2$
5	3 h. 15 min.	∞	1 h. 35 min.	3 h. 15 min.	1 h. 35 min.	3 h. 15 min.	$16^1/_2$
6	2 h. 30 min.	∞	55 min.	2 h. 30 min.	55 min.	2 h. 30 min.	$18—18^1/_2$

The experiments cannot be compared quantitatively, owing to small differences in age, treatment etc. of the roots. The roots from *A*, *B* and *C* belonging to the same experiment. however, are perfectly comparable. The sign ∞ means that at the end of the experiment the roots did not show any curvature. Stimulating intermittently I, therefore, found no influence of the inverse vertical position on the reaction-time which was, however, considerably lengthened by stimulating in the ordinary longitudinal direction.

I repeated these experiments with (unstimulated) secondary roots. The results were about the same i.e. the roots in *B* and *C* began to react simultaneously. Those in *A*, however, could not be induced to react even by changing the intervals to 2 : 1. I carried out some special experiments to study this point with considerably more material but even after 12—20 hours all the rootlets remained straight.

Could I have found an accelerating action of the inverse longitudinal force in my main roots?

According to Miss VON UBISCH the inverse longitudinal force strengthens a preceding transverse stimulus as much as an equal transverse force would do. LUNDEGÅRDH gives as presentation-time for the main roots 5 min. (at 26° C.; at 18—20° C. it will be still more). To reach this presentation-time by stimulating 3 min.—1 min. *C* requires 20 min., *B* 5 min., this makes a difference of 15 min. in the reaction-time.

This estimate is, of course, rough and probably too low. But my method was surely sufficiently sensitive to ascertain a difference as large as this.

The result of my experiments, therefore, is that an evidently retarding influence of the longitudinal force has been found, whereas I failed to find an accelerating influence of the inverse longitudinal force.

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Chemistry. — *Osmosis of ternary liquids. General considerations* II. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 29, 1927).

The changes in concentration of the liquids; normal and anormal apparent osmosis.

If the liquids of the osmotic system

$$L \mid L' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

travel along the osmosis-path, then the concentrations of the substances X Y and W change every moment. If we only consider the concentration of each of those substances separately, without considering them in their mutual relation, then we might draw conclusions from this, which would sometimes be absolutely in variance with reality.

For it is impossible to deduce only from the change of the concentration of one of the substances, in which direction this substance diffuses through the membrane; for this we have to know the change of the concentration of *all* substances.

As, in examining the osmosis, the changes in the concentrations of liquids are most striking, we shall discuss them first; with this we shall at the same time have occasion to point at some examples of this apparent osmosis.

If we assume, to concentrate our thoughts, the liquid on the left side of the membrane has a smaller amount of X than the right side liquid, we can distinguish the following cases.

a. The amount of X of the left side liquid becomes greater and that of the right side liquid becomes smaller. We represent this by the signs:

$$\uparrow < \downarrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

The sign $<$ indicates that the left side liquid has a smaller amount of X then the right side liquid. The left side arrow $\uparrow$ which is pointed upwards indicates that the amount of X of the left side liquid increases; the right side arrow $\downarrow$ which is pointed downwards indicates that the amount of X of the right side liquid decreases.

b. The X-amount of both liquids increases; we represent it by:

$$\uparrow < \uparrow^{*} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

The meaning of it is clear now. To the meaning of the sign $*$ near the right arrow we shall refer later on.

c. The X-amount of both liquids decreases; we represent it by:

$$*\downarrow < \downarrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

d. The X-amount of the left side liquid becomes still smaller and that of the right side liquid becomes still greater; we represent it by:

$$*\downarrow < \uparrow * \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

In following considerations we shall discuss experimental examples of such cases.

Now we shall say:

A. the X-amount of a liquid changes *normally*.

1. if it increases, when the liquid on the other side of the membrane has a greater amount of X;

2. if it decreases, when the liquid on the other side of the membrane has a smaller amount of X;

B. the X-amount of a liquid changes *anormally*.

1. if it increases, although the liquid on the other side of the membrane has a smaller amount of X;

2. if it decreases, although the liquid on the other side of the membrane has a smaller amount of X.

Applying this to the cases, mentioned above sub *a*—*d*, we see that on the side where we find the asterisk, the X-amount changes anormally; on the side where this sign * is not found, the X-amount changes normally.

In case a both liquids change normally; we now shall say that the system changes normally-normally.

In case *b* the left side liquid changes normally but the right side liquid anormally; consequently the system changes: normally-anormally.

In case *c* we shall say that the system changes anormally-normally and in case *d* that the system changes anormally-anormally.

Of course the words normal and anormal should not lead us to look upon the one phenomenon a more normal than the other.

All we have discussed above as regards the X-amount of a liquid is valid of course also for its amount of Y and W.

In order to illustrate what has been discussed just now, we take the system (1). We assume that the liquid L contains only the substances W and Y and the liquid L' only W and X. Then liquid L is represented by a point 1 on the side WY and liquid L' by a point 1′ on the side WX of fig. 1.

We assume that curve 1 e 1′ is the osmosis-path of the system; the liquids travel along this path in the direction of the arrows.

Each line, drawn through point *e*, which intersects the osmosis-path, is a conjugation line; its points of intersection represent conjugated liquids. The lines 1 . 1′, 3 . 3′ and 4 . 4′ must therefore also go through

point e. The dashes at the letters m, a, b and c indicate where we have to imagine those points on the path; consequently we imagine the points m', a' and b' on branch $2'.3'$ and point c' on branch $3'.4'$.

We shall begin by considering the change of the X-amount of the liquids.

In point 1 the X-amount of the liquid L is zero; as it travels along the path $1.e$ in the direction of the arrows, its X-amount increases all the time during the osmosis and it approaches that of the terminating liquid e.

In point $1'$ the X-amount of the liquid L' is represented by the length of the line $W1'$; as it travels along the path $1'.e$, its amount of X decreases all the time and it approaches also that of the terminating-liquid e.

Although all this may be read easily from fig. 1, we shall yet represent it in another diagram, by which we get a better survey also in more

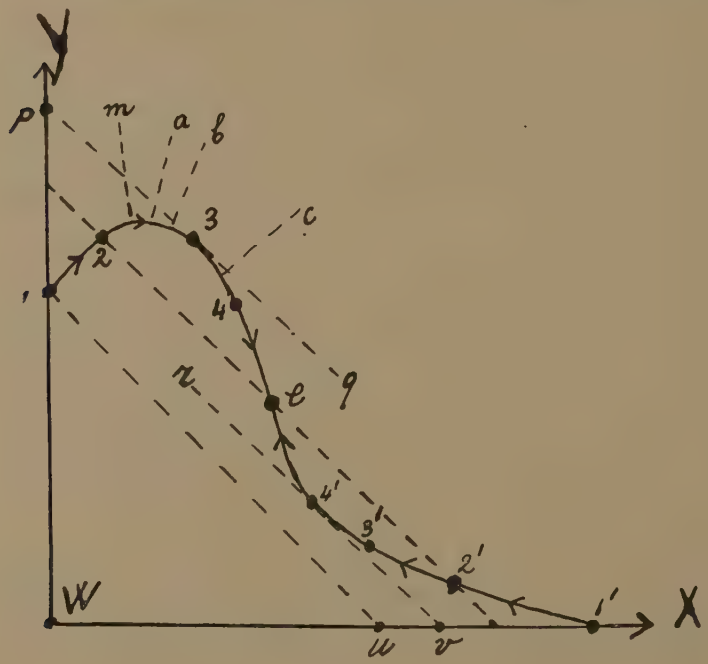

Fig. 1.

difficult cases; for this we take fig. 2 in which on the vertical axis has been drawn the X-amount and on the horizontal axis the time t of the osmosis; we shall call this the $X.t$-diagram of the system.

At the time $t=0$ viz. at the moment that the osmosis begins, L is

found in point 1 of fig. 1 and so its X-amount is zero; consequently it is represented in fig. 2 by a point 1 which coincides with point 0.

After a certain time t_2 L is found in point 2 of its path; if in fig. 2 we draw on the horizontal axis this time t_2 and on the vertical axis the X-amount, then we obtain also a point 2 in this diagram.

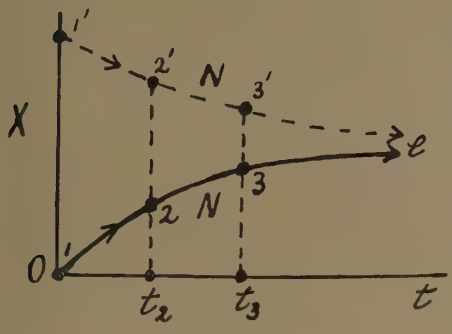

Fig. 2.

Acting in the same way with the other liquids of the path 1 . e in fig. 1 we get curve 1 . 2 . 3 . e. As the liquid L reaches the point e theoretically after an infinitely long time, point e is situated at infinite distance. We call this curve the X—L-path.

If we do the same for the liquid L' we get the curve 1'. 2'. 3'. e of fig. 2. At the moment that the osmosis begins, consequently when $t = 0$, the liquid L' is found viz. in the point 1' of fig. 1 and its X-amount is represented, therefore, by the length of the line $W1'$. If in fig. 1 and fig. 2 we express the X-amount in the same unities of length, then $01'$ must be $= W1'$; this has however been neglected in this and following sketch-figures.

We call this curve 1'. 2'. 3'. e the X—L'-path; point e of this path is situated also at infinite distance; consequently the X—L- and the X—L'-path approach one another asymptotically.

In order to facilitate the survey of these and subsequent figures, we shall draw the L-path and dot the L'-path.

From those paths it appears that we can represent the change of the X-amount by

$$\uparrow < \downarrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the left side liquid has during the total osmosis a smaller X-amount than the right side liquid; it also appears from fig. 2 that the X-amount of the left side liquid increases continually and that of the right side liquid decreases. Consequently we may say that the system has a normal X—L- and X—L'-path; this is indicated in fig. 2 by the letter N. The total system changes its X-amount normally—normally.

As, according to (2), the X-amount of the left side liquid increases and that of the right side liquid decreases, we should perhaps be inclined to infer that the substance X diffuses through the membrane from right to left; we shall represent this by:

$$L \mid L' \longleftarrow X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For this conclusion, however, is not the least foundation; it may be

right or it may be wrong; we shall soon refer to a similar case, in which this is clearly shown.

We now take the Y-amount of the liquids. When liquid L is found in point 1 of fig. 1 then its Y-amount is represented by the length of the line $W.1$. In travelling along the path this Y-amount at first increases till point m and afterwards decreases in order to approach that of the liquid e; consequently in point m the Y-amount is a maximum.

If we draw in an $Y.t$-diagram (fig. 3) on the vertical axis the Y-amount of the liquids L and on the horizontal axis the time t of the osmosis, then we get a curve $1.2.m.3.e$ which has a maximum in the point m at the time t_m. We call this curve the Y—L-path.

If the liquid L' is found in point $1'$ of its path in fig. 1, then its Y-amount is zero. As this increases continually during the osmosis from point $1'$ till point e, we get, therefore, in fig. 3 a curve $1'.2'.m'\,3'.e$ which has nothing particular in point m'. We call this curve the Y—L'-path.

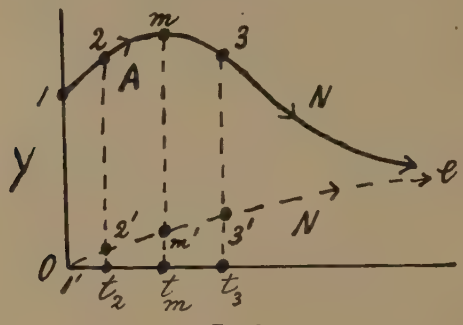

Fig. 3.

It now appears from the figure that we can represent the change of the Y-amount of both liquids, as long as they are found on the branches $1.m$ and $1'.m'$ of their paths, by

$$*\uparrow > \uparrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the sign $>$ indicates that the left liquid has a greater Y-amount than the right liquid. We see from fig. 3 that the Y-amount of both liquids increases on those branches; as the Y-amount of the left liquid increases, although the right liquid has a smaller Y-amount, it changes, therefore, anormally. This is indicated in (4) by the sign $*$; in fig. 3 the letter A is written beside this branch, the letter N beside the other.

If the liquids are found on the branches $m\,e$ and $m'\,e$ of their path in fig. 3, then we can represent the change of their Y-amount by:

$$\downarrow > \uparrow \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore both liquids change their Y-amount normally on those branches; this is indicated in fig. 3 by the letter N. It now appears from (4) and (5):

the Y—L-path consists of an anormal branch $1.m$ and a normal branch $m.e$;

the Y—L'-path develops normally all the time.
the system changes its Y-amount.
on branch $1 . m$ (and $1'. m'$) anormally-anormally.
on branch $m . e$ (and $m'. e'$) normally-normally.

We shall represent the system which is formed by the conjugated liquids 2 and 2′ by:

$$L_2 \mid L_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We now may put the question: in which direction does the substance Y diffuse through the membrane?

For the change of the Y-amount of those liquids scheme (4) is valid; we see from this that the Y-amount increases on both sides of the membrane, so that it is clear that no conclusion can be made with respect to the direction in which the substance Y really diffuses through the membrane. For the change of the Y-amount is only a seeming osmosis and not only the result of the diffusion of the substance Y alone, but also of that of the other substances. Later on we shall see that the substance Y really diffuses according to the scheme:

$$L_2 \mid L_2' \longrightarrow Y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

viz. from left to right.

All this is clear without further explications if we take the system:

$$L_1 \mid L_1' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which the right side liquid contains no Y. During the osmosis the substance Y must diffuse from left to right and yet the Y-amount on the left side of the membrane still increases.

In order to deduce the change of the W-amount of the two liquids we first return to the osmosis-path in fig. 1. In this we can draw a conjugation-line $2\,e\,2'$ through point e; this line runs parallel to the side $X\,Y$ of the triangle, which not has been drawn; in point 3 the tangent $p\,q$ has been drawn parallel to this side and in point 4′ the tangent $r\,v$; also the line $1 . u$ runs parallel to this side.

The points of the line $1 . u$ represent liquids, which all have the same W-amount; the same is true for all lines, which run parallel to $X\,Y$, consequently for $r\,v$, $2 . 2'$ etc. As, however, the line $1 . u$ is situated closer to the anglepoint W than the line $r\,v$, the liquids of $1 . u$ have a greater W-amount than those of the line $r\,v$; the latter having again a greater W-amount than those of the line $2 . 2'$ etc. Hence follows:

of all liquids of the L-path (curve $1 . 2 . e$) the liquid in point 3 has the smallest W-amount; this increases from point 3 as well towards 1 as towards e; the W-amount is, therefore, a minimum in point 3;

of all liquids of the L'-path (curve $1'. 2'. e$) the liquid in point 4′ has the greatest W-amount; this decreases from this point as well towards 1′ as towards e; the W-amount is, therefore, a maximum in point 4′.

There exist two conjugated liquids viz. 2 and 2′ which have the same W-amount; this is equal to that of the termination-liquid e.

Now it is easy to draw the path of the liquid L in a W. t-diagram; this is represented in fig. 4 by curve 1 . 2 . 3 . 4 . e which has a minimum in point 3.

The path of the liquid L' which must have a maximum in point 4′ is represented by the curve 1′. 2′. 3′. 4′. e. It appears from fig. 1 that the liquid 1 has a greater W-amount than the liquid 1′; consequently in fig. 4 point 1 must be situated over point 1′.

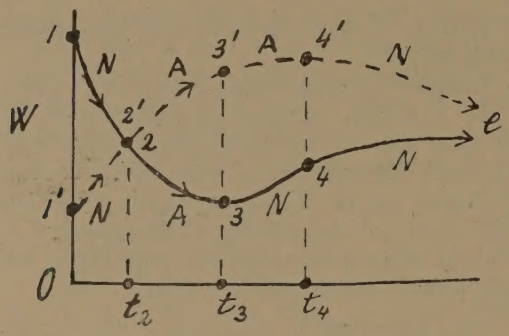

Fig. 4.

As we have seen above, the conjugated liquids 2 and 2′ have the same W-amount; consequently the L- and L'-path must intersect one another in fig. 4 in a point, which represents the W-amount of those liquids 2 and 2′. As this W-amount is equal to that of the terminating-liquid e, a horizontal line, drawn through this point of intersection must go through the point e situated at infinite distance.

We now divide the L-path into the four branches 1 . 2, 2 . 3, 3 . 4 and 4 . e and the L'-path of course into the corresponding branches 1′. 2′, 2′. 3′, 3′. 4′ and 4′. e. We now can represent the change of the W-amount of the liquids by the following scheme:

$$\begin{array}{ccccccc} 1.2 & & 2 & & 2.3 & 3.4 & 4.e \\ \downarrow > \uparrow & & *\downarrow = \uparrow* & & *\downarrow < \uparrow* & \uparrow < \uparrow* & \uparrow < \downarrow \end{array} \quad . \; . \; . \quad (9)$$

From this scheme we can learn the same things as from fig. 4. We see among other things that:

on the left side of the membrane the W-amount is greater in the beginning of the osmosis (branch 1 . 2) but afterwards smaller than on the right; in point 2 it becomes equal on both sides,

on the left side of the membrane the W-amount decreases in the beginning of the osmosis (branches 1 . 2 and 2 . 3), afterwards it increases;

on the right side of the membrane the W-amount increases in the beginning of the osmosis (branches 1 . 2, 2 . 3 and 3 . 4); afterwards it decreases.

On branch 2 . 3 the W-amount of both liquids changes anormally, for the smallest W-amount here still decreases and the greater still increases.

In point 2 both liquids have the same W-amount; as this does change, we shall call this also anormal.

On branch 3.4 the W-amount of the left side liquid changes normally, that of the right side liquid anormally.

Consequently we may also say:

the W—L-path consists of a normal part (1.2), an anormal part (2.3) and afterwards again of a normal part (3.4 and 4.e);

the W—L'-path consists of a normal part (1'.2'), an anormal part (2'.3' and 3'.4') and afterwards again of a normal part (4'.e);

the W-amount of the system changes:

on branch 1.2 (and 1'.2') normally—normally
„ „ 2.3 (and 2'.3') anormally—anormally
„ „ 3.4 (and 3'.4') normally—anormally
„ „ 4.e (and 4'.e) normally—normally.

We may learn all this easily as well from fig. 4 as from scheme (9).

After the previous considerations it is evident that we can draw no conclusions from the change of the W-amount of the liquids with respect to the direction in which the substance W diffuses through the membrane. Later on we shall see in which way we can deduce this direction.

We can summarise in a single scheme all that we have discussed above and what we have deduced from the figs. 1—4. As in the following communication also the points a, b and c on the path come under discussion, we include them also in the branches given.

	X	Y	W
1.2	$\uparrow < \downarrow$	$^*\uparrow > \uparrow$	$\downarrow > \uparrow$
2	„	„	$^*\downarrow = \uparrow^*$
2.m	„	„	$^*\downarrow < \uparrow^*$
m.a.b.3	„	$\downarrow > \uparrow$	„
3.c.4	„	„	$\uparrow < \uparrow^*$
4.e	„	„	$\uparrow < \downarrow$

. . . (10)

Here is indicated on which side of the membrane each substance has its greatest concentration, if this increases or decreases during the osmosis, if those changes are normal or anormal, etc.

From this we may read all that has been represented in figs. 1—4 and deduced from them, so that this scheme might be substituted for the figs. 1—4. Afterwards we shall sometimes use it.

Later on in the experimental part we shall discuss examples of the systems, mentioned above, which are being examined in collaboration with Mr. B. C. VAN BALEN WALTER.

Leiden, Lab. of Inorg. Chem. (*To be continued*).